FILE COPY ONLY

PIBS 3716 E

ENVIRONMENTAL RESEARCH

ECOLOGICAL INTEGRATION OF ZEBRA MUSSELS IN THE GREAT LAKES: TROPHIC INTERACTIONS AND IMPACTS ON CONTAMINANT DYNAMICS

FINAL REPORT

RAC Project No. 666G

MINISTRY OF ENVIRONMENT AND ENERGY

Ontario

ISBN 0-7778-4977-1

ECOLOGICAL INTEGRATION OF ZEBRA MUSSELS IN THE GREAT LAKES: TROPHIC INTERACTIONS AND IMPACTS ON CONTAMINANT DYNAMICS

FINAL REPORT

RAC Project No. 666G

Report prepared by:

Hugh J. MacIsaac, PhD, G. Douglas Haffner, PhD,
Jan J. Ciborowski, PhD
Department of Biological Sciences and
Great Lakes Institute for Environmental Studies
University of Windsor

FEBRUARY 1996

Cette publication technique n'est disponible qu'en anglais.
Copyright: Queen's Printer for Ontario, 1996

This publication may be reproduced for non-commercial purposes with appropriate attribution.

PIBS 3416E

ACKNOWLEDGEMENT AND DISCLAIMER

This report was prepared for the Ontario Ministry of Environment and Energy as part of a Ministry funded project. The views expressed in this report are those of the author and do not necessarily reflect the views and policies of the Ministry of Environment and Energy, nor does mention of trade names or commercial products constitute endorsement or recommendation for use. The Ministry, however, encourages the distribution of information and strongly supports technology transfer and diffusion.

Any person who wishes to republish part or all of this report should apply for permission to do so to the Environmental Research Program, Science and Technology Branch, Ontario Ministry of Environment and Energy, 135 St. Clair Avenue West, Suite 100, Toronto, Ontario, Canada, M4V 1P5.

Table of Contents

Executive Summary 2
Overview of the study 3
Acknowledgements 6

Chapter 1 - Calibration of Dreissena polymorpha as a biomonitor 7
    Abstract 7
    Introduction 7
    Methods 11
    Results 15
    Discussion 18
    Conclusion 22
    References 23
    Tables 28
    Figures 33
Chapter 2 - Food uptake of PCBs by Dreissena polymorpha 41
    Abstract 41
    Introduction 42
    Methods 44
    Results 48
    Discussion 51
    References 53
    Tables 56
    Figures 60
Chapter 3 - Diet and contaminant profiles of lower Great Lakes' waterfowl 63
    Abstract 63
    Introduction 65
    Methods 67
    Results 71
    Discussion 75
    References 78
    Table 83
    Figures 84
    Appendix 97

Executive Summary

1) Elimination rate constants (k_2) for field-exposed Dreissena polymorpha for 36 PCB congeners ranged between 0.172 and 0.042 (day^{-1}). Elimination rate constants declined significantly with increasing chemical octanol-water partition coefficient (i.e. log K_{ow}). By contrast, time to 95% steady-state was positively associated with log K_{ow}, ranging between 17.5 and 71 days.

2) Total bioavailable PCB concentration, which ranged between 0.054 to 0.662 ng/L, increased from Lake St. Clair to western Lake Erie sites. Marked heterogeneity existed between sites with respect to concentrations of most organocontaminants profiled.

3) Analysis of laboratory uptake rates of nine PCB congeners revealed an inverse relationship between uptake rate and chemical log K_{ow}.

4) Waterfowl collected from sites in the lower Detroit River (Fighting Island) and western Lake Erie were analyzed for diet and organocontaminant concentrations. Waterfowl with a non-Dreissena diet (e.g. macrophytes and snails) had significantly lower concentrations of most contaminants relative to con- and heterospecific individuals that fed on zebra mussels. Waterfowl from western Lake Erie consumed exclusively (lesser scaup) or mainly (greater scaup, bufflehead) Dreissena, and had higher concentrations of most contaminants relative to conspecifics from Fighting Island with a similar diet (greater and lesser scaup). Contaminant concentrations were highest in greater scaup. Principal component analysis revealed that chemical profiles of Dreissena-consuming waterfowl were very similar but significantly different from those of waterfowl that avoided Dreissena.

5) In summary, Dreissena polymorpha appears to have excellent potential as a biomonitor of PCBs. Contaminant concentrations of mussels collected from lower Great Lakes sites appear consistent with environmental exposure. In addition, zebra mussels contaminated with organic compounds may serve as an important exposure route in taxa for which it is a major food source.

Overview of the Study

The Great Lakes currently support at least 139 nonindigenous species (Mills et al. 1993). The zebra mussel Dreissena polymorpha is among the most recent species to invade the Great Lakes (Hebert et al. 1989). Zebra mussels achieve extraordinary population densities in the lower Great Lakes, including in western Lake Erie and in Lake St. Clair (Mackie 1991; Leach 1993). As siphonate bivalves, dreissenid mussels feed by drawing water through the mantle cavity and filtering a broad range (1 - 1200 μm) of suspended particles on gill and palp surfaces (Ten Winkel and Davids 1982; Sprung and Rose 1988). Given its high population densities and moderate per capita filtering rates, the zebra mussel has the ability to dramatically alter seston standing stocks and energy flow, particularly in shallow systems (e.g. see MacIsaac et al. 1992; Nicholls and Hopkins 1993).

Zebra mussels also have the potential to alter contaminant cycling in invaded lakes. For example, Mersch et al. (1992) employed D. polymorpha as a biomonitor of trace metals, radionuclides and organic contaminants in the Mosel River (France and Germany). Zebra mussels are a conduit for contaminants and energy to high trophic levels by serving as prey for crayfish, fish and waterfowl (e.g. see MacIsaac 1994; Wormington and Leach 1992). de Kock and Bowmer (1992) observed that European tufted ducks fed zebra mussels contaminated with a wide assortment of PCBs suffered from reproductive failure owing to smaller clutch sizes, lower egg hatch rates and an elevated incidence of nest abandonment by adults, relative to control ducks fed non-contaminated Dreissena.

The purpose of this study was to assess the suitability of D. polymorpha as an organic contaminant biomonitor in the lower Great Lakes (Erie and St. Clair) by determining depuration and uptake rates. In addition, considering the dominance of benthic communities by Dreissena and European reports of significant bioaccumulation by the mussel, this study also addresses the importance of Dreissena to waterfowl diets and organocontaminant body burdens.

Specific objectives are described in each chapter.

Overview References

de Kock, W.C. and C.T. Bowmer. 1992. Bioaccumulation, biological effects, and food chain transfer of contaminants in the zebra mussel (Dreissena polymorpha). pp. 503-533 In T.F. Nalepa and D.W. Schloesser (eds.), Zebra Mussels. Biology, impacts, and control. Lewis Publishers, Boca Raton, Florida.

Hebert, P.D.N., B.W. Muncaster and G.L. Mackie. 1989. Ecological and genetic studies on Dreissena polymorpha (Pallas): a new mollusc in the Great Lakes. Can. J. Fish. Aquat. Sci. 46: 1587-1591.

Leach, J.H. 1992. Impacts of the zebra mussel (Dreissena polymorpha) on water quality and fish spawning reefs in western Lake Erie. pp. 381-397 In T.F. Nalepa and D.W. Schloesser (eds.), Zebra Mussels. Biology, impacts, and control. Lewis Publishers, Boca Raton, Florida.

MacIsaac, H.J. 1994. Size selective predation on zebra mussels (Dreissena polymorpha) by crayfish (Orconectes propinquus). J. North Amer. Benth. Soc. 13:206-216.

MacIsaac, H.J., W.G. Sprules, O.E. Johannsson and J.H. Leach. 1992. Filtering impacts of larval and sessile zebra mussels (Dreissena polymorpha) in western Lake Erie. Oecologia 92:30-39.

Mackie G.L. 1991. Biology of the exotic zebra mussel, Dreissena polymorpha, in relation to native bivalves and its potential impact in Lake St. Clair. Hydrobiol. 219:251-268.

Mersch, J., A. Jeanjean, H. Spor and J.C. Pihan. 1992. The freshwater mussel Dreissena polymorpha as a biomonitor for trace metals, organochlorines and radionuclides. pp. 227- 244, In: The zebra mussel Dreissena polymorpha. D. Neumann and H.A. Jenner (eds.)., Gustav Fischer, Stuttgart.

Mills E.L., J.H. Leach, J.T. Carlton and C.L. Secor. 1993. Exotic species in the Great Lakes: a history of biotic crises and anthropogenic introductions. J. Great Lakes Res. 19:1-54.

Nicholls, K.H. and G.J. Hopkins. 1993. Recent changes in Lake Erie (north shore) phytoplankton: cumulative impacts of phosphorus loading reductions and the zebra mussel introduction. J. Great Lakes. Res. 19:637-647.

Sprung, M. and U. Rose. 1988. Influence of food size and food quantity on the feeding of the mussel Dreissena polymorpha. Oecologia 77: 526-532.

Ten Winkel, E.H. and C. Davids. 1982. Food selection by Dreissena polymorpha Pallas (Mollusca: Bivalvia). Freshwat. Biol. 12: 553-558.

Wormington, A. and J.H. Leach. 1992. Concentrations of migrant ducks at Point Pelee National Park, Ontario, in response to invasion of zebra mussels, Dreissena polymorpha. Can. Field Nat. 106:376-380.

Acknowledgements

This study was supported by an Ministry of Environment and Energy Research Advisory Council grant (#666G) to H.J. MacIsaac, G.D. Haffner and J.J.H. Ciborowski. Chapter three (contaminant accumulation in waterfowl) was co-sponsored by a research grant from the Canadian Wildlife Service. Katy Haralampides, Geoff Riddle and the staff of the GLIER analytical laboratory provided excellent field and laboratory assistance. Dr. Bak Chauhan, grant liaison officer, provided assistance and guidance. Chapters 1 (biomonitor calibration of zebra mussels) and 3 (biomagnification of organocontaminants in Dreissena-consuming waterfowl) represent University of Windsor Ph.D. and M.Sc. thesis contributions by Heather Morrison and Ed Mazak, respectively, whereas work described in chapter 2 (Dreissena uptake kinetics) was conducted by postdoctoral fellow Yves Couillard.

CHAPTER 1

Calibration and use of zebra mussels (Dreissena polymorpha) to estimate bioavailable organic chemical concentrations in water

Abstract

Zebra mussels (Dreissena polymorpha Pallas), with shell lengths ranging from 1.0 to 1.5 cm, were used to estimate organochlorine bioavailability at nine sites in Lake St. Clair, the Detroit River and western Lake Erie. The elimination kinetics of 36 PCB congeners, ranging in octanol/water partition coefficients (log K_{OW}) from 5.60 to 7.36, were determined. Elimination rate constants (k_2), based on lipid-normalized data, ranged from 0.172 to 0.042 days-1 and revealed a significant ($p < 0.01$) negative relationship with increasing log K_{OW}. Time to 95% steady-state (t_{95}) ranged from 17.5 to 71.0 days and depended directly on logK_{OW}. Total bioavailable PCB concentrations (Aroclor 1254:1260 equivalents) ranged from 0.054 ng/L (Puce and Leffler Drain, Lake St. Clair) to 0.662 ng/L (Middle Sister Island, Lake Erie). Contaminant levels in zebra mussels from the nine sites differed significantly ($p<0.01$) from one another as did estimates of bioavailable chemical concentrations. Even in the well-mixed western Lake Erie, Arochlor 1254:1260 equivalents ranged from 0.311 to 0.662 ng/L.

Introduction

Despite numerous studies assessing organic contaminant concentrations in biota (Haffner et al. 1994; Suns et al. 1993; Hebert and Haffner 1991; Muncaster et al. 1989; Ciborowski and Corkum 1988; Pugsley et al. 1985), little information is known about bioavailable chemical concentrations in aquatic ecosystems. Currently, accurate techniques for directly measuring bioavailable chemical are not available as extraction techniques remove chemical from different phases in water. Relating these measurements to bioavailable chemical concentrations is difficult. Concentrations of dissolved organic matter (DOM) and particulate organic matter (POM) are known to greatly influence the bioavailability of organic chemicals (Fisher et al. 1993; Knulst 1992; Day 1991; Johnsen et al. 1989; Black and McCarthy 1988). Hydrophobic organic contaminants readily sorb to POM and DOM and the complex of organic chemical and POM or DOM is too large to passively diffuse across biological membranes. As a result, chemicals in the DOM or POM phase are not available to be bioconcentrated by organisms. Since DOM and POM concentrations fluctuate, direct single point in time measurements are unlikely to provide reliable estimates of mean bioavailable chemical concentrations. Quantitative biomonitors are considered to provide the best estimates of chemical bioavailability in natural systems (Gobas and Zhang 1994) because they provide a time integrated measure of contaminant availability to organisms, and are much more sensitive to trace contaminants than direct measurement techniques.

The zebra mussel Dreissena polymorpha Pallas possesses many qualities that predispose it as a good biomonitor in the Great Lakes. These qualities include its abundance, widespread distribution and sessile nature. Other beneficial qualities arise from the mussel's planktivorous feeding habit and high filtering capacity. It has been observed that organisms occupying lower trophic positions primarily accumulate organic chemicals from the freely dissolved phase (Connolly and Pedersen 1988; Thomann 1981; Macek et al. 1979). The freely dissolved phase is thought to be the most important exposure route for organic chemicals to filter feeders living in mesotrophic to oligotrophic waters, where POM and DOM concentrations are low. Consequently, bioavailable chemical concentrations based on mussel body burdens are likely to best reflect exposure to freely dissolved chemical.

To use zebra mussels as a quantitative biomonitor, it is necessary to integrate biological properties such as size and filtering rate with physical/chemical properties of the contaminants. When this complex relationship is modelled the most important kinetic parameter, in terms of its role in the bioaccumulation of chemicals, is the elimination rate constant (k_2)(Landrum et al. 1992, Gobas et al. 1988). The rate at which hydrophobic chemicals are eliminated by an organism determines both the time to chemical equilibrium between the organism and its environment as well as the bioaccumulation potential. As a result, elimination rate constants can be used to estimate uptake rate constants (k_1), bioconcentration factors (BCFs) and time to steady-state.

Once the kinetics of an organic contaminant in zebra mussels have been established chemical concentrations in mussel tissues can be related to bioavailable concentrations in the environment over a specific period of time. Toxic organic chemicals are a serious pollutant in Lake St. Clair, the Detroit River and Lake Erie (Bolsenga and Herdendorf 1993; Furlong et al. 1988; EC and EPA 1988; Hartig and Thomas 1988). Polychlorinated biphenyls (PCBs), octachlorostyrene (OCS), hexachlorobenzene (HCB) and p,p'-DDE are of particular concern in this region because they are prevalent, persistent and harmful to biota (Carter and Hites 1992; Strachan and Eisenreich 1988; Oliver and Pugsley 1986).

The objectives of this study are to 1) determine the elimination rate constants for PCBs in zebra mussels and 2) estimate bioavailable chemical concentrations of PCB congeners ranging in log K_{OW} from 5.6 to 7.4 and 3) compare concentrations of PCBs and five other organic contaminants in the Huron-Erie corridor.

Calibration of zebra mussels

Elimination model

The elimination of PCBs by zebra mussels via the gills and faeces can be as described as:

$$dC_m/dt = -(k_2C_m + k_eC_m) \quad (1)$$

where C_m (µg/kg lipid) is the concentration of chemical in the mussel, t is time (days), k_2 (-days) is the rate constant for elimination to water via the gills, and k_e (-days) is the rate constant for elimination via faeces (Gobas et al. 1988). Implicit in this model are several assumptions, including; the lipid phase of the organism is the predominant sink for PCBs; the volume of lipid within the organism remains constant over time; food and water contain no chemical during depuration; chemical transfer between the organism and its environment is passive; there is no biotransformation or metabolism; depuration kinetics can be described by first-order rate constants. Currently, in zebra mussels there is no evidence to suggest that metabolic degradation is a significant process for the PCBs measured in this study. Molluscs are known for having extremely low levels of microsomal mono-oxygenases which are enzymes capable of metabolizing most organic compounds (Walker 1987).

If mussels have an initial PCB burden, are not producing faeces and, are not subsequently exposed to PCBs, Equation 1 can be integrated such that:

$$C_{mt} = C_{m0}(e^{-k_2t}) \quad (2)$$

where, C_{mt} is the concentration of PCB in mussels at a given time and, C_{m0} is the concentration of PCB in mussels at time zero.

Using measured k_2 values, the time it takes zebra mussels to achieve 95% steady-state levels of PCBs (t_{95}) can be calculated as follows:

$$t_{95} = -\ln 0.05/k_2 \quad (3)$$

Model for calculating bioavailable chemical concentrations

The chemical activity or fugacity (f) of any phase in the environment is defined as the concentration of chemical (C) divided by the fugacity capacity (Z) of the phase:

$$f = C/Z \quad (4)$$

At steady-state the ratio of the fugacity of any two phases approaches one. Consequently, the ratio of the fugacity of an organism (fm) to the fugacity of water (fw) can be expressed as;

$$f_m / f_w = C_m Z_w / C_w Z_m = 1 \quad (5)$$

The octanol-water partition coefficient (K_{OW}) represents the ratio of chemical concentrations in octanol and water when the fugacities of chemical in each phase are equal. The octanol-water partition coefficient equals the ratio of the fugacity capacities of the two phases:

$$K_{OW} = Z_o / Z_w \quad (6)$$

Octanol is used as a lipid surrogate. Assuming the fugacity capacity of octanol equals lipid (Connolly and Pedersen, 1988), K_{OW} equals the ratio of the fugacity capacity of an organism's lipid and water:

$$K_{OW} = Z_m / Z_w \quad (7)$$

Bioavailable water concentrations are then calculated from an organisms chemical burden as follows:

$$C_w = C_m / K_{OW} \quad (8)$$

where, C_w is the average bioavailable water concentration during the time it takes the mussel to achieve steady-state with their environment, C_m is the lipid-normalized chemical concentration in the mussels, and K_{OW} is the octanol-water partition coefficient for the chemical of interest. The equation assumes that lipid is the primary sink for PCBs and that zebra mussels are in steady-state with their environment.

Methods

Elimination experiment

Zebra mussels were collected from a relatively clean site (Arochlor 1254:1260 mean + s.e. = 679.90 + 18.45 µg/kg lipid) and separated randomly into two groups. One group was transported to an area of high PCB contamination (Trenton Channel;

Furlong et al. 1988) and the second group was held in the laboratory in charcoal filtered water. After two days, the transplanted contaminated (Arochlor 1254:1260 mean + s.e. = 8829.18 + 642.953 µg/kg lipid) mussels were brought to the laboratory and were placed in four aquaria.

The relatively uncontaminated mussels were placed in the same aquaria as experimental mussels to act as internal controls. The controls accounted for extraneous sources of PCBs and internal recycling of PCBs among mussels.

Aquaria were held in one of two growth chambers for the duration of the experiment. Temperatures were measured daily in each of the growth chambers and averaged (+ 1 s.e.) 13.4 + 0.24 °C and 13.5 + 0.26 °C over the 16 day experiment. There was no mortality of zebra mussels after their transfer to the laboratory nor during the course of the experiment. Within a few hours after transfer, mussels were actively filtering.

Control (clean) zebra mussels and contaminated zebra mussels were removed from each aquaria on days 0, 1, 2, 4, 8 and 16. Mussels, with shell lengths greater than 1 cm, were shucked, wrapped in hexane rinsed aluminum foil and frozen until analysis. Upon completion of the elimination study, three samples of water from each aquaria and each filter were examined for veligers under a dissecting microscope (Zeiss Jena Technival 2) at 125x magnification.

During the experiment, mussels were left fastened to their original substrate. The mussels and substrate were rinsed before being placed in aquaria. In order to reduce stress on the mussels, entire rocks, containing enough zebra mussels to provide at least 3 g of tissue, were removed on collection days.

Elimination data were corrected for ambient PCB exposures by subtracting the PCB concentration in control mussels from the PCB concentration in treatment mussels on each collection day. Thus, estimates of k_2 are considered to represent depuration to 'PCB-free' water.

All log K_{OW} values were taken from Shiu and Mackay (1986) except congeners #110, #182/187, #180 and #170/190 which were cited from Hawker and Connell (1988).

Field collections

Zebra mussels were collected from four sites in western Lake Erie (Middle Sister Island, Colchester Reef, Hen Island and East Sister Island; Figure 1.1). Mussels were also collected from Lake St. Clair (Grosse Point, Leffler Drain, Puce and Stoney Point) and Detroit River (Belle Isle and Grosse isle) sites.

Mussels were scraped off infested rocks and sorted into four size classes based on shell length. The size classes were < 1.0 cm, 1.0-1.5 cm, 1.5-2.0 cm and > 2.0 cm. After sorting, the mussels were shucked and their soft tissues were wrapped in hexane rinsed aluminum foil and frozen until analysis.

Chemical analysis

Preparation and clean-up of tissue samples followed the methods of Lazar et al. (1992). Tissue samples were randomly sorted before being taken to the laboratory. Approximately 3 g wet weight of zebra mussel tissue were homogenized with 20 g Na_2SO_4. The mixture was transferred to a glass column containing 10 mL of Na_2SO_4. and eluted with 300 mL of DCM/hexane (1:1)(pesticide grade). The extract was roto-evaporated to 5 mL in preparation for clean-up. Extracts were transferred into 1 X 35 cm glass columns containing 6 g Florisil (60-100 µm mesh) and 2 cm anhydrous Na_2SO_4. The column was eluted with 50 mL of hexane. Recovered solvent was roto-evaporated to 2 mL. Organic contaminants were quantified using gas chromotography electron capture detection (GC-ECD). The detection level was 0.05 µg/kg and recoveries were greater than 90%. Canadian Wildlife Service (CWS) standards and reference material were analyzed every tenth sample and blanks were run every six samples.

The % lipid was determined using preparatory extracts from the tissue samples. The extracts were diluted with hexane until they reached a volume of 25 mL. Two milliliters of well-mixed solution were removed and placed in a preweighed beaker. The beaker was placed in an oven at 100 °C for at least 1 hr. The beaker was reweighed. The % lipid was calculated using the equation:

$$\% \text{ lipid} = W1/Wt \times Vt/Ve \times 100$$

where, W1 is the weight of lipid, Wt is the total weight of the sample extracted, Vt is the total volume of extract and, Ve is the total volume of extract used for lipid determination.

Statistical Analysis

Elimination experiment

Estimates of elimination rate constants (k_2) were calculated using linear regression (SAS Inst. Inc. 1985). The significance of linear regression relationships were determined using one-way ANOVAs (Zar 1984). Student's t-tests were calculated according to Zar (1984).

Between site comparison:

Concentrations of contaminants in zebra mussels with shell lengths ranging from 1.0 - 1.5 cm, were reported on a wet weight basis, for each site. In order to accommodate statistical comparisons of contaminant burdens between sites, principal component (PC) analysis was used to reduce the number of variables (i.e. contaminants). Contaminants containing a large proportion of non-detectable concentrations were removed from the PC analysis along with contaminants with distributions that were non-linear or non-normal. Inclusion of a variable within a component required a loading of at least 0.70 with no other loading of greater that 0.32. From the loading matrix, factor scores were calculated for each sample. Analysis of variance (ANOVA) and Tukey's multiple comparisons were performed using the factor scores to compare the contaminant burdens of zebra mussels from different sites. Analyses were performed using Systat (1992).

Results

Elimination experiment

Figure 1.2 illustrates the monophasic decline in lipid-normalized chemical concentrations, over the course of the experiment, for some of the congeners. Concentrations declined rapidly and continuously. By day 16, many congeners were approaching steady-state. The elimination rate constants ranged from 0.172 d^{-1} (PCB#64) to 0.042 d^{-1} (PCB# 183) (Table 1.1) and declined significantly as $\log K_{OW}$ increased (ANOVA, $r^2=0.59$, $p<0.01$, $n=36$) (Figure 1.3). Time to 95% steady-state is also summarized in Table 1.1. The t_{95} values ranged from 17.5 to 71.0 days and increased with increasing $\log K_{OW}$.

Although mussels were not fed during the experiment, they exhibited no change in % lipid between day 0 and day 16 ($t= 3.182$, $p= 0.668$, $n= 8$). Additionally, examination of water indicated that no veligers were released during the experiment.

Between site comparisons

The % lipid of zebra mussels were similar at all sites except Grosse Point and Angstrom Park (Table 1.2). Mussels from Grosse Point had higher average % lipid levels and mussels from Angstrom Park had lower average % lipid levels than the other sites.

Zebra mussels collected from all nine sites had detectable levels of PCBs and other organochlorine compounds (Figure 1.4). The four western Lake Erie sites, Colchester Reef, Middle Sister Island, Hen Island and East Sister Island and Grosse

Point on the U.S. side of Lake St. Clair contained the highest organochlorine concentrations. The Grosse Point site contained exceptionally high concentrations of p,p'-DDE and the lower chlorinated PCB congeners. The three Lake St. Clair and the upper Detroit River sites, located on the Canadian shore, were the least contaminated.

The PC analysis grouped the contaminants onto three components which accounted for 88 % of variance in contaminant concentrations among samples (Table 1.3). The first component (PC-1) explained 50 % of total variance and was highly positively correlated with concentrations of 13 high log K_{OW} PCBs. PC-2 accounted for 29 % of the total variance and was positively correlated with low K_{OW} PCBs such as #70, #74 and p,p'-DDE. The third factor (PC-3) explained 9 % of the variation in contaminant concentrations among samples and was positively associated with HCB and OCS which have a single source in the St. Clair River.

Contaminant concentrations in zebra mussels differed significantly among the nine sites. These differences were reflected in the site-to-site variation in mean factor scores ($p < 0.0001$). The most contaminated sites with respect to the PCB congeners represented by PC-1 were Middle Sister Island, Grosse Point, Hen Island, East Sister Island and Colchester Reef. Middle Sister Island and Hen Island had the highest concentrations of these congeners and differed significantly ($p< 0.001$) from every other site. Grosse Point and East Sister Island had the second highest concentrations and differed significantly from the other sites ($p< 0.001$). Colchester Reef had the third highest concentrations and differed significantly ($p< 0.001$) from the other sites. The four relatively uncontaminated Lake St. Clair and upper Detroit River sites, located on the Canadian side, did not differ from one another but all differed significantly ($p< 0.001$) from the heavily contaminated western Lake Erie and Grosse Point sites.

PC-2 represented PCBs# 70, 74 and p,p'-DDE. Grosse Point had the highest levels of p,p'-DDE and high levels of PCBs #70 and #74. PC-2 scores differed between Grosse Point and all other sites ($p < 0.05$) except East Sister Island and

Stoney Point which also had relatively high p,p'-DDE, PCBs #70 and #74. Stoney Point differed significantly from Angstrom Park and Colchester Reef ($p < 0.05$).

PC-3 represented the organochlorines HCB and OCS. Zebra mussels from the Puce site had the highest concentrations of HCB and OCS and differed significantly, with respect to PC-3 ($p < 0.001$), from all other sites.

Size-class comparisons

The contaminant concentrations were compared on a lipid-normalized basis in order to reduce variation caused by the inclusion of shells in the chemical analysis of the < 1 cm size class. Figure 1.5 shows the concentrations of 37 PCB congeners in the four size classes from Colchester Reef and East Sister Island. From this figure, it is evident that the largest size class, > 2.0 cm, had the highest mean congener concentrations and the greatest variability of any of the size classes. The smallest size class, < 1.0 cm, had the lowest mean concentrations. In order to assess the relative concentrations of lower and higher K_{OW} congeners between size classes, PCB #52, that loaded on PC-2, was chosen to represent lower K_{OW} congeners. PCB #138, a dominant congener in Arochlor 1254 and 1260, was chosen to represent higher K_{OW} congeners of component 1 (Figure 1.6). Concentrations of PCB #52 were very similar among the four size classes at both the Colchester Reef and East Sister Island sites, whereas concentrations of #138 were substantially lower in the < 1.0 cm size class than in the larger size classes. Concentrations of #138 were more variable among size classes at the East Sister Island site than at the Colchester Reef site.

Bioavailable chemical concentrations

Table 1.1 lists bioavailable PCB congener concentrations (calculated from equation 8) for each site. Based on Arochlor 1254:1260, Middle Sister Island was the most contaminated site (0.662 ng/L) and Puce and Leffler Drain were the least contaminated sites (0.054 and 0.009 ng/L respectively). Concentrations ranged from less than 0.0005 ng/L to 0.349 ng/L at Middle Sister Island and from less than 0.0005 ng/L to 0.083 ng/L and 0.192 ng/L at Puce and Leffler Drain, respectively. These bioavailable chemical concentrations represent the mean concentration during the period of time it took zebra mussels to reach steady-state. In this study, time to steady-state was approximated by time to 95% steady-state (Table 1.1).

Discussion

Rapid PCB kinetics enable zebra mussels to quickly achieve steady-state with their environment and to closely track fluctuations in environmental chemical concentrations. The elimination rate constants estimated in this study provided information on factors affecting PCB accumulation in mussels. The rapid monophasic depuration of PCBs indicated that the soft tissues of the mussel behaved as a homogeneous unit with regard to the release of individual congeners. Elimination of lipophilic chemicals was also observed to be monophasic in zebrafish (Brachydanio rerio) (Fox et al. 1994), fish, molluscs, daphnids (Hawker and Connell 1988) and blue mussels (Mytilus edulis) (Pruell et al. 1986). Hence, PCB elimination by zebra mussels is adequately described by one-compartment, first-order kinetic models.

Elimination rates measured in this study were primarily via the gills, as mussels did not produce faeces or veligers and, exhibited no change in % lipid between day 0 and day 16 of the experiment. Even without these additional means to depurate chemical, elimination rate constants were strikingly similar to in situ elimination rate constants measured in zebra mussels (Yankovich and Haffner, in prep.) and green-lipped mussels (Perna viridis) (Tanabe et al. 1987) and much more rapid than elimination rate constants measured in fish (Fox et al. 1994; Oliver and Niimi 1985)

Fisher et al. (1993) measured the elimination rate constant for PCB #153 as 0.096 d^{-1} (wet weight) with zebra mussels in the laboratory. To compare their results with this study, the elimination rate constant (k_2) for PCB #153 was recalculated on a wet weight basis (mean + standard error: 0.038 + 0.007 (d^{-1})).

The octanol/water partition coefficient ($\log K_{OW}$) described 59% of the variation in elimination rate constants. Hydrophobicity is concluded to be the primary factor influencing the elimination rates of PCBs, but other factors such as temperature (Fisher et al. 1993; Farrington 1975), filtering rate, reproductive state and general health (Farrington 1975) can also regulate elimination rate constants.

Tanabe et al. (1987) found that $\log K_{OW}$ described 50% of the variation in k_2 constants. A negative linear relationship between $\log K_{OW}$ and k_2 has also been observed in fish (Hawker and Connell 1988; Konemann and van Leeuwen 1980) and zebra mussels (Fisher et al. 1993). A significant relationship between $\log K_{OW}$ and k_2 supports the conclusion that partitioning between water and lipid is the primary process governing the accumulation of PCBs. Since partitioning is a good descriptor of PCB kinetics, PCB concentrations be best expressed on a lipid-normalized basis when discussing kinetic parameters (Tanabe et al. 1987).

Since organic contaminants preferentially partition into lipid, differences in the % lipid in mussels from different sites could partially account for differences in contaminant levels. In this study lipid-normalizing the data did not change the relationship in contaminant burdens between mussels from the different sites.

Despite lower percent lipid levels, the four western Lake Erie sites contained high concentrations of PCBs, especially highly chlorinated (PC-1) PCBs. Inputs of chemical from the Detroit River largely account for the high PCB concentrations observed in zebra mussels. Since Detroit River-derived chemicals are mostly particle-bound (Carter and Hites 1992), these contaminant profiles most likely reflect exposure to sediment-derived PCBs. The spatial heterogeneity in mussel contaminant burdens within the basin probably reflect depositional gradients.

Zebra mussels from Grosse Point in Lake St. Clair also contained high concentrations of PCBs. Unlike western Lake Erie, the Grosse Point mussels contained high concentrations of the lower chlorinated (PC-2) PCBs. Since lower chlorinated PCBs do not persist in the environment as long as higher chlorinated PCBs, this congener profile suggests exposure to an active local source of PCB contamination.

Of the chemicals represented by PC-2, p,p'- DDE was found in the highest concentrations. Although this DDT metabolite was prevalent at every site, the four Lake St. Clair sites had the highest concentrations. The level of p,p'- DDE was especially elevated at Grosse Point and Stoney Point. These areas are predominantly used for agriculture. Historic applications combined with runoff from farm land could contribute to elevated concentrations observed at these sites (Russell et al. 1995). QCB, HCB and OCS are released from known point sources on the St. Clair River. It was expected that Lake St. Clair zebra mussels would have higher concentrations of these chemicals than the Detroit River and western Lake Erie mussels. In fact, zebra mussels from eight of the nine sites had similar levels of these chemicals. Only Puce, on Lake St. Clair, had exceptionally high levels of QCB, HCB and OCS. Zebra mussels from the Puce site were collected at the mouth of the Puce River, and it is difficult to explain why concentrations of these chemicals would be especially high at this site.

Significant differences in contaminant concentrations were only detected between zebra mussels with shell lengths < 1.0 cm and those with shell lengths > 1.0 cm for the high K_{OW} congeners (Figure 1.5). Zebra mussels representing size classes larger than 1.0 cm had very similar contaminant concentrations to one another. The time to 95% steady-state for the PCBs measured in this study ranged from 16.0 to 71.0 days and depended directly on log K_{OW}. It is likely that many mussels from the < 1.0 cm size class were less than two months old and had not reached steady-state concentrations with the environment. Additionally, differences in growth rates between the size classes could result in differences in lipid-normalized contaminant burdens. The greater variability in the > 2 cm size class may be due to the inclusion of older mussels whose filtering rate is declining. Fisher et al. (1993) found that chemical uptake clearance rates and filtering rates were closely related. Chevreuil and Testard (1991) also found no significant difference in organochlorine concentrations between adult zebra mussels with shell lengths > 1.0 cm.

We have not explored whether lipid levels in Dreissena fluctuate seasonally in association with mussel spawning activities. Bruner et al. (1994) reported that mussels with high lipid content had greater uptake rates for hexachlorobiphenyl and benzo(a)pyrene than low-lipid Dreissena. However, no studies have linked spawning activity with changes in uptake or depuration kinetics. If reproduction-induced changes in lipid levels affect these kinetics, reproductive status of mussels employed as biomonitors would require assessment. Reproductive status of female mussels can, however, be scored (1-4) with relative ease based on the developmental stage of ova in ovarian follicles (MacIsaac, pers. obs).

At every site, bioavailable concentrations of the lower chlorinated PCBs were greater than the higher chlorinated PCBs. Lower chlorinated PCBs are less hydrophobic and therefore more likely to remain in the freely dissolved phase than higher chlorinated PCBs. Since the freely dissolved phase is a major chemical exposure route to mussels, differences between bioavailable chemical concentrations of lower and higher chlorinated congeners not only reflects differences in the congener make-up of original PCB mixtures released into the environment, but also differences in freely dissolved concentrations of these congeners.

Bioavailable chemical concentrations were spatially heterogeneous even in well-mixed systems like western Lake Erie. This spatial heterogeneity was especially pronounced for the higher chlorinated congeners relative to congeners with fewer substitutes chlorine atoms. The consequence of decades of PCB loading into western Lake Erie from the Detroit River is exceptionally high bioavailable concentrations of the most persistent, highly chlorinated PCB congeners.

Zebra mussels are very sensitive biomonitors. Bioavailable concentrations of PCB congeners in the order of 0.0005 ng/L were quantified using mussels. Techniques for directly measuring chemicals in water are rarely able to quantify concentrations less that 0.05 ng/L (Maguire et al. 1993; Swackhamer and Armstrong 1987; Fox et al. 1983) and this sensitivity is only achieved after processing large quantities of water. The ability to measure small concentrations of bioavailable chemical in the environment is very important since the most hydrophobic chemicals are very difficult to detect using direct measurement techniques but have the greatest potential to bioaccumulate. Use of accurate, reliable methods for assessing environmental concentrations of chemicals available to biota is important when evaluating water quality. The ability of zebra mussels to track dilute chemical concentrations renders them excellent biomonitors.

Conclusion

Zebra mussels are very sensitive biomonitors of bioavailable environmental chemicals. When deployed as biomonitors of PCB congeners at nine sites in the Lake St. Clair-Lake Erie corridor, bioavailable PCB congener concentrations ranged from less than 0.0005 ng/l to 0.568 ng/l. Chemical concentrations in mussels varied significantly between sites. The PCB congener concentrations observed in zebra mussels offshore of Grosse Point Michigan were indicative of an active local source of PCBs. The Puce collection site located in relatively uncontaminated Canadian shore of Lake St. Clair had exceptionally high levels of HCB and OCS that are difficult to explain. The most contaminated region in the Lake St. Clair-Lake Erie corridor was western Lake Erie. Although the western basin is well mixed, there was significant between site heterogeneity in zebra mussel body burdens and bioavailable chemical concentrations. This study demonstrates the usefulness of zebra mussels as both a quantitative and descriptive monitor of organochlorine pollution. Additionally, this study identifies the significant between site heterogeneity in bioavailable chemical concentrations within the Lake St. Clair-Lake Erie corridor. Since zebra mussels are found in abundance throughout southeastern Canada and the continental United States (Nalepa and Schloesser 1992), are easy to collect and provide site-specific information on contaminant loadings, mussels are an excellent means for assessing chemical exposure concentrations to organisms in the environment.

References

Black, M. C. and J. F. McCarthy. 1988. Dissolved organic macromolecules reduce the uptake of hydrophobic organic contaminants by the gills of rainbow trout (Salmo gairdneri). Environ. Toxicol. Chem. 7:593-600.

Bolsenga, S. J. and Herdendorf, C. E. 1993. Lake Erie and Lake St. Clair Handbook. Wayne State University Press. Detroit, Michigan.

Bruner, K.A., S.A. Fisher and P.F. Landrum. 1994. The role of the zebra mussel, Dreissena polymorpha, in contaminant cycling: I. The effect of body size and lipid content on the bioconcentration of PCBs and PAHs. J. Great Lakes Res. 20:725-734.

Carter, D. S. and Hites, R. A. 1992. Fate and transport of Detroit River derived pollutants throughout Lake Erie. Environ. Sci. Technol. 26:1333-1341.

Chevreuil, M. and Testard, P. 1991. Emploi d'un lamellibranche filtreur (Dreissena polymorpha Pallas) pour l'evaluation des pollutions organochlorees (PCB, pesticides). Hydrologie. 312:473-477.

Ciborowski, J. H. and L. D. Corkum. 1988. Organic contaminants in adult aquatic insects of the St. Clair and Detroit Rivers, Ontario, Canada. J. Great Lakes Res. 14:148-156.

Connolly, J. P. and C. J. Pedersen. 1988. A thermodynamic-based evaluation of organic chemical accumulation in aquatic organisms. Environ. Sci. Technol. 22:99-103.

Day, K. E. 1991. Effects of dissolved organic carbon on accumulation and acute toxicity of fenvalerate, deltamethrin and cyhalothrin to Daphnia magna (Straus). Environ. Toxicol. Chem. 10:91-101.

Environment Canada, U.S. Environmental Protection Agency, Ontario Ministry of the Environment, and N.Y. Department of Environmental Conservation. 1988. Joint evaluation of upstream/downstream Niagara River monitoring data for the period April 1986 to March 1987.

Fisher, S.W., D.C. Gossiaux, K.A. Bruner, and P.F. Landrum. Investigations of the toxicokinetics of hydrophobic contaminants in the zebra mussel (Dreissena polymorpha). In: T.F. Nalepa and D.W. Schloesser [eds.] Zebra mussels: biology, impacts, and control. Lewis Publishers. Ann Arbor. Mich. Ch. 28.

Farrington, J. 1975. Bioaccumulation of hydrophobic organic pollutants. In F. Moriarty. [ed.] Organochlorine Insecticides: Persistent organic pollutants. Academic Press. London.

Fox, M. E., J. H. Carey and B. G. Oliver. 1983. Compartmental distribution of organochlorine contaminants in the Niagara River and the western basin of Lake Ontario. J. Great Lakes Res. 9:287-294.

Fox K., G. P. Zauke and W. Butte. 1994. Kinetics of bioconcentration and clearance of 28 polychlorinated biphenyl congeners in Zebrafish (Brachydanio rerio). Ecotoxicol. Environ. Saf. 28:99-109.

Furlong, E. T., Carter, D. S. and Hites, R. A. 1988. Organic contaminants in sediments from the Trenton Channel of the Detroit River, Michigan. J. Great Lakes Res. 14:489-501.

Gobas, F. A. P. C., R. Russell and G. D. Haffner. 1988. Biomonitoring: Chemical dependent quantitative relationships for the body burdens of organic chemicals in aquatic organisms. Proc. Tech. Transfer. Conf. OMOE Toronto. ISSN 0840-8440.

Gobas, F. A. P. C. and X. Zhang. 1994. Interactions of organic chemicals with particulate and dissolved organic matter in the aquatic environment. In: J. L. Hamelink, P. F. Landrum, H. L. Bergman and W. H. Benson. Bioavailability: Physical, Chemical, and Biological Interactions. Lewis Publ. Ann Arbor. Ch. 2.

Haffner, G. D., M. Tomczak and R. Lazar. 1994. Organic contaminant exposure in the Lake St. Clair food web. Hydrobiologia. 281:19-27.

Hartig, J.H. and R. L. Thomas. 1988. Development of plans to restore degraded areas in the Great Lakes. Env. Managem. 12:327-347.

Hawker, D.W. and D. W. Connell. 1988. Octanol-water partition coefficients of polychlorinated biphenyl congeners. Environ. Sci. Technol. 22:382-387.

Hebert, C.E. and G.D. Haffner. 1991. Habitat partitioning and contaminant exposure in cyprinids. Can. J. Fish. Aquat. Sci. 48:261-266.

Johnsen, S., J. Kukkonen and M. Grande. 1989. Influence of natural aquatic humic substances on the bioavailability of benzo(a)pyrene to Atlantic salmon. 81/82:691-702.

Knulst, J. C. C. 1992. Effects of pH and humus on the availability of 2,2',4,4',5,5'-hexachlorobiphenyl-14C in lake water. Environ. Toxicol. Chem. 11:1209-1216.

Konemann, H. and K. van Leeuwen. 1980. Toxicokinetics in fish: accumulation and elimination of six chlorobenzenes by guppies. Chemosphere. 9:3-19.

Landrum, P. F., T. D. Fontaine, W. R. Faust, B. F. Eadie and G. A. Lang. 1992. Modelling the accumulation of polycyclic aromatic hydrocarbons by the amphipod Diporeia. In F. A. P. C Gobas and J. A. McCorquodale [eds.] Chemical dynamics in fresh water ecosystems. Lewis Publ. Ann Arbor. Ch. 7.

Lazar, R., R.C. Edwards, C.D. Metcalfe, T. Metcalfe, F.A.P.C. Gobas and G.D. Haffner. 1992. A simple, novel method for the quantitative analysis of coplanar (non-ortho substituted) polychlorinated biphenyls in environmental samples. Chemosphere. 25:493-504.

Macek, K. J., Petrocelli, S. and Sleight, B. H. 1979. Considerations in assessing the potential for, and significance of, biomagnification of chemical residues in aquatic food chains. In L. L. Marking and R. A. Kimerle, eds. Aquatic Toxicology: Second Symposium. ASTM STP 67. American Society for Testing and Materials, Philadelphia, PA, pp.251-268.

Muncaster, B. W., Innes, D. J., Hebert, P. D. N. and Haffner, G. D. 1989. Patterns of organic contaminant accumulation by freshwater mussels in the St. Clair River, Ontario. J. Great Lakes Res. 15:645-653.

Maguire, J. R., R. J. Tkacz and S. P. Batchelor. 1993. Extraction efficiencies of hydrocarbons from Niagara River water. Environ. Toxicol. Chem. 12:805-811.

Nalepa, T. A. and D. W. Schloesser. 1992. Zebra mussels: biology, impacts, and control. CRC Press, Inc., Boca Raton, Florida. pp.810.

Oliver, B.G. and A.J. Niimi. 1985. Bioconcentration factors of some halogenated organics for rainbow trout: Limitations in their use for prediction of environmental residues Environ. Sci. Technol. 19:842-849.

Oliver, B. G. and C. W. Pugsley. 1986. Chlorinated contaminants in St. Clair River sediments. Water Poll. Res. J. Canada. 21:785-790.

Pruell, R.J., J.L. Lake, W.R. Davis and J.G. Quinn. 1986. Uptake and depuration of organic contaminants by blue mussels (Mytilus edulis) exposed to environmentally contaminated sediment. Marine biology. 91:497-507.

Pugsley, C. W., Hebert, P. D. N., Wood, G. W., Brotea, G. and Obal, T. W. 1985. Distribution of contaminants in clams and sediments from the Huron-Erie corridor. I-PCBs and octachlorostyrene. J. Great Lakes Res. 11:275-289.

Russell, R. W., R. Lazar and G. D. Haffner. 1995. Biomagnification of organochlorines in Lake Erie white bass. Environ. Toxicol. Chem. In press.

SAS Institute Inc. 1985. User's Guide: Statistics, 5 ed. SAS Inst. Inc., Cary, N.C.

Shiu, W. Y. and D. Mackay. 1986. A critical review of aqueous solubilities, vapor pressures, Henry's Law constants, and octanol-water partition coefficients of the polychlorinated biphenyls. J. Phys. Chem. Ref. Data. 15:911-928.

Strachan, W. M. and S. J. Eisenreich. 1988. Mass Balancing of toxic chemicals in the Great Lakes: the role of atmospheric deposition; Report to the International Joint Commission on Great Lakes Water Quality: Windsor, ON, Canada,

Suns, K. R., G. G. Hitchin and D. Toner. 1993. Spatial and temporal trends of organochlorine contaminants in spottail shiners from selected sites in the Great Lakes (1975-1990). J. Great Lakes Res. 19:703-714.

Swackhammer, D. L. and D. E. Armstrong. 1987. Distribution and characterization of PCBs in Lake Michigan water. J. Great Lakes Res. 13:24-36.

Systat. 1992. version 5.01.Systat Inc., Evanston, IL, USA, 60201.

Tanabe, S., R. Tatsukawa and D.J.H. Phillips. 1987. Mussels as bioindicators of PCB pollution: A case study on uptake and release of PCB isomers and congeners in green-lipped mussels (Perna viridis) in Hong Kong waters. Environ. Pollut. 47:41-62.

Thomann, R. V. 1981. Equilibrium model of fate of microcontaminants in diverse aquatic food chains. Can. J. Fish. Aquat. Sci. 38:280-296.

Walker, C.H. 1987. Kinetic models for predicting bioaccumulation of pollutants in ecosystems. Environ. Pollut. 44:227-240.

Zar, J.H. 1984. Biostatistical Analysis, second edition. Prentice-Hall, Englewood Cliffs, N.J.

Table 1.1. Elimination rate constants (k_2), time to 95% steady-state (t_{95}) and mean bioavailable congener concentrations based on mean tissue concentrations in zebra mussels collected from the nine study sites. S.P. is Stoney Point, P. is Puce, L.D. is Leffler Drain, G.P. is Grosse Point, A.P. is Angstrom Park, C.R. is Colchester Reef, M.S.I. is Middle Sister Island, E.S.I. is East Sister Island and H.I. is Hen Island.

Table 1.2. Number of composite samples and mean % lipid (+ s. d.) from nine sites in Lake St. Clair, the Detroit River and Lake Erie.

Table 1.3. Component loadings and % of total variance explained by each component from the Principle Components analysis on organic chemical concentrations from the nine sites.

Figure 1.1. Location of collection sites.

Figure 1.2. The concentration of various PCB congeners (mean + s.e.) in *Dreissena polymorpha* during the elimination period.

Figure 1.3. Elimination rate constants (k_2) (mean + s.e.) versus octanol-water partition coefficients ($\log K_{OW}$) for PCB congeners in *Dreissena polymorpha* (n=36).

Figure 1.4. Mean contaminant concentrations (+ s.e.) in zebra mussels (shell length 1.0-1.5 cm) from the nine sampling locations.

Figure 1.5. Mean contaminant concentrations (+ s.e.) in zebra mussels from four size classes (n=3) collected at East Sister Island and Colchester Reef.

Figure 1.6. Mean concentrations (+ s.e., n = 3) of PCB #52 ($\log K_{OW} = 6.10$) and PCB #138 ($\log K_{OW} = 6.83$) in 4 size classes from Colchester Reef and East Sister Island.

Table 1.1.

					Mean Bioavailable Chemical Concentrations (ng/l)								
Congener	logKow	k2 (d-1)	+/- s.e.	t 95 (d)	B. P.	P.	L. D.	G. P.	A. P.	C. R.	M. S. I.	E. B. I.	H. I.
28	5.80	0.145	0.0120	20.7	0.019	0.022	0.024	0.171	0.015	0.045	0.117	0.057	0.072
31	5.60	0.145	0.0120	20.7	0.124	0.076	0.160	0.503	0.156	0.162	0.349	0.148	0.258
52	6.10	0.107	0.0157	28.0	0.052	0.048	0.028	0.061	0.043	0.035	0.079	0.130	0.049
49	6.10	0.100	0.0089	30.0	0.020	n.d.	n.d.	0.041	n.d.	0.006	0.032	n.d.	0.025
44	6.00	0.099	0.0167	30.2	0.010	0.001	0.005	0.019	0.002	0.009	0.025	0.034	0.012
42	5.60	0.154	0.0342	19.5	0.409	n.d.	0.192	0.325	0.098	0.032	0.155	0.568	0.050
64	6.10	0.172	0.0307	17.5	0.113	0.024	0.085	0.099	0.043	0.030	0.073	0.149	0.048
74	6.10	0.101	0.0087	29.6	0.095	0.036	0.075	0.169	0.048	0.103	0.224	0.184	0.156
70	5.90	0.107	0.0124	28.0	0.070	0.083	0.076	0.133	0.076	0.083	0.097	n.d.	0.074
66/95	5.80	0.089	0.0136	33.7	0.055	0.050	0.039	0.087	0.033	0.084	0.158	0.101	0.120
101	6.40	0.100	0.0125	30.0	0.056	0.008	0.008	0.020	0.006	0.018	0.029	0.041	0.031
99	6.60	0.092	0.0056	32.6	0.014	0.010	0.011	0.024	0.009	0.021	0.033	0.038	0.033
97	6.60	0.106	0.0224	28.4	0.022	0.014	0.019	0.044	0.014	0.041	0.072	0.054	0.067
87	6.50	0.097	0.0162	30.9	0.043	0.009	0.006	0.026	0.008	0.038	0.078	0.054	0.051
110	6.48	0.093	0.0095	32.2	0.059	0.029	0.029	0.092	0.037	0.188	0.275	0.182	0.231
151	6.90	0.084	0.0055	35.9	0.005	n.d.	0.010	0.016	0.001	n.d.	0.028	n.d.	n.d.
118	6.40	0.068	0.0084	44.1	0.035	0.028	0.038	0.081	0.036	0.159	0.324	0.223	0.216
146	6.90	0.061	0.0041	49.0	n.d.	0.003	0.004	0.009	0.002	0.013	0.023	n.d.	0.020
153	6.90	0.047	0.0081	63.2	0.013	0.002	0.003	0.006	0.002	0.011	0.020	0.012	0.015
105	6.40	0.065	0.0046	46.3	0.065	0.038	0.045	0.101	0.046	0.149	0.324	0.178	0.229
138	7.00	0.078	0.0084	38.6	0.007	0.004	0.004	0.011	0.006	0.023	0.049	0.026	0.027
129	7.30	0.098	0.0126	30.5	0.003	0.001	0.001	0.002	0.001	0.005	0.011	0.005	0.006
182/187	7.17	0.052	0.0033	58.2	n.d.	n.d.	<0.0005	<0.0005	n.d.	0.001	0.001	0.001	0.001
183	7.00	0.042	0.0032	71.0	0.002	0.007	0.002	0.008	0.003	0.019	0.033	0.017	0.022
185	7.00	0.070	0.0048	42.9	<0.0005	0.002	<0.0005	0.003	n.d.	0.007	0.009	0.005	0.006
174	7.00	0.052	0.0079	57.6	<0.0005	<0.0005	<0.0005	<0.0005	n.d.	0.005	0.005	0.003	0.004
171	6.70	0.058	0.0010	51.8	n.d.	<0.0005	n.d.	<0.0005	n.d.	0.003	0.006	0.003	0.005
200		0.054	0.0075	55.7									
172		0.053	0.0096	57.0									
180	7.36	0.060	0.0029	50.2	0.002	0.001	0.001	0.002	0.001	0.004	0.008	0.005	0.006
170/190	7.27	0.057	0.0057	52.5	0.001	<0.0005	<0.0005	0.001	<0.0005	0.003	0.007	0.003	0.004
201	7.50	0.057	0.0060	52.9	n.d.	n.d.	n.d.	0.002	<0.0005	0.001	0.002	0.001	0.001
203	7.10	0.051	0.0061	58.6	0.002	<0.0005	<0.0005	0.002	n.d.	0.003	0.007	0.002	0.005
195	7.10	0.051	0.0144	58.8	n.d.	0.001	n.d.	0.001	n.d.	0.001	0.003	0.002	0.003
194	7.10	0.053	0.0034	56.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
206	7.20	0.046	0.0175	65.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Arochlor 1254:1260					0.095	0.054	0.054	0.149	0.081	0.311	0.662	0.351	0.365
Arochlor 1260					0.018	0.009	0.009	0.018	0.009	0.035	0.07	0.044	0.053

Table 1.2.

Site	# of Composite Samples	Mean % Lipid	+/- S. E.
Puce	2	2.18	0.19
Leffler Drain	3	1.77	0.03
Stoney Point	3	1.57	0.10
Grosse Point	4	3.77	0.27
Angstrom Park	5	1.02	0.06
Hen Island	3	1.66	0.10
Colchester Reef	3	1.47	0.05
East Sister Island	3	1.24	0.04
Middle Sister Island	2	1.47	0.02

Table 1.3.

Congener #	Component-1	Component-2	component-3	
180	0.983	0.146	-0.006	
201	0.977	0.141	0.005	
203	0.975	0.160	-0.005	
170	0.958	0.230	0.056	
182	0.956	0.199	0.101	
174	0.950	0.077	0.251	
153	0.943	0.235	0.050	
149	0.941	0.300	0.013	
171	0.937	0.137	0.160	
138	0.925	0.300	0.149	
194	0.917	0.162	0.062	
183	0.903	0.308	-0.153	
200	0.891	-0.027	0.273	
146	0.877	0.374	-0.174	
129	0.815	0.397	0.221	
141	0.790	0.450	-0.220	
110	0.780	0.473	0.292	
151	0.755	0.564	-0.099	
105	0.755	0.191	0.433	
101	0.751	0.562	0.301	
87	0.670	0.572	0.303	
66	0.634	0.737	0.162	
99	0.544	0.753	0.274	
70	0.102	0.958	0.050	
74	0.072	0.928	-0.120	
pp'-DDE	0.026	0.873	0.312	
transnonachlor	0.056	0.848	0.415	
64	0.446	0.793	0.144	
97	0.420	0.785	-0.174	
44	0.359	0.762	0.297	
31	0.166	0.758	0.417	
49	0.481	0.686	0.457	
52	0.417	0.633	0.489	
60	0.151	0.561	0.594	
HCB	-0.148	0.171	0.864	
OCS	0.097	0.170	0.538	
% of total				Sum
variance explaine	50.24	28.54	9.32	88.12

Figure 1.1

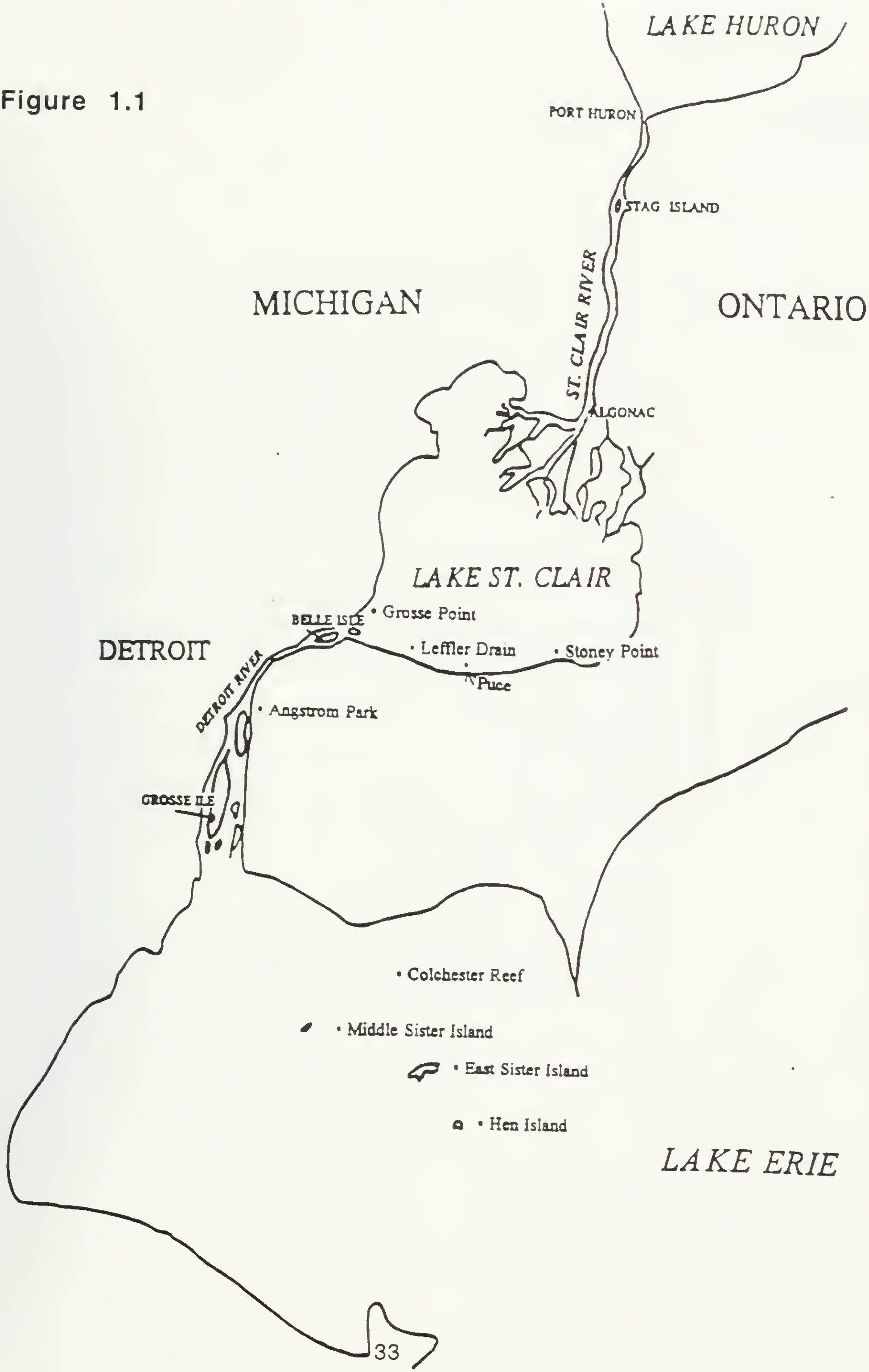

LAKE HURON
PORT HURON
STAG ISLAND
MICHIGAN
ST. CLAIR RIVER
ONTARIO
ALGONAC
LAKE ST. CLAIR
BELLE ISLE
Grosse Point
DETROIT
Leffler Drain
Stoney Point
Puce
DETROIT RIVER
Angstrom Park
GROSSE ILE
Colchester Reef
Middle Sister Island
East Sister Island
Hen Island
LAKE ERIE

Figure 1.2

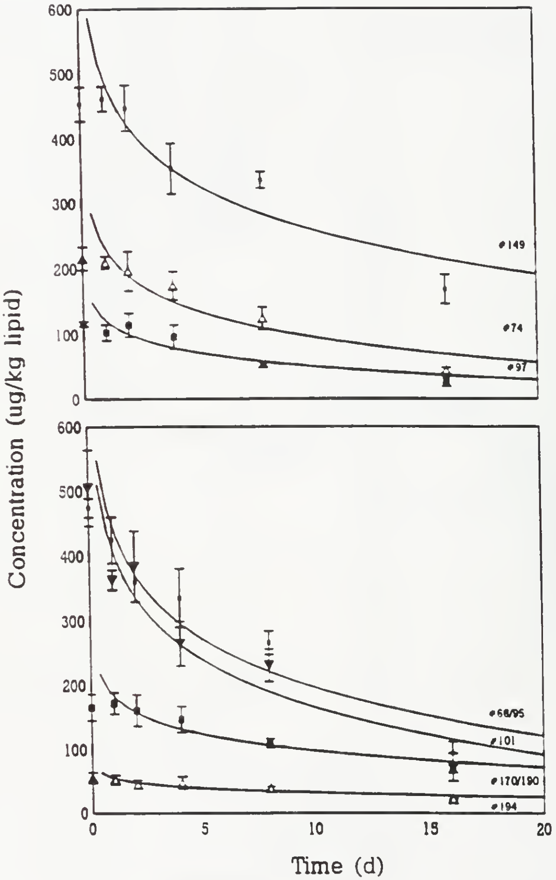

600
500
400
300
200
100
0
#149
#74
#97
600
500
400
300
200
100
0
#68/95
#101
#170/190
#194
0
5
10
15
20
Concentration (ug/kg lipid)
Time (d)

Figure 1.3

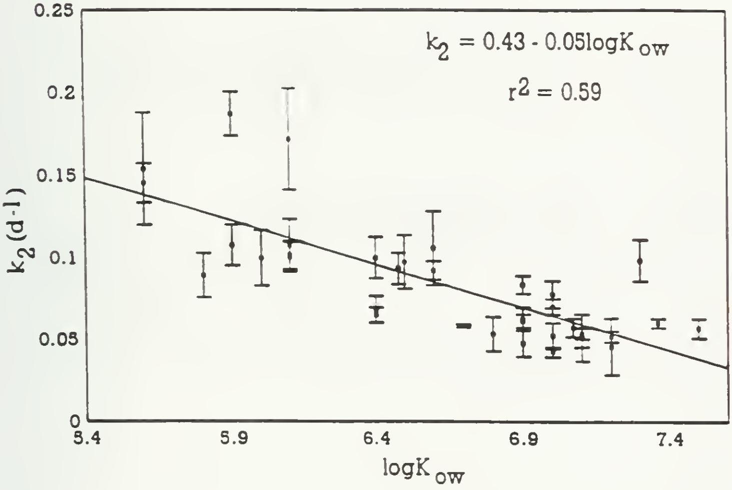

$k_2 = 0.43 - 0.05\log K_{ow}$
$r^2 = 0.59$
0.25
0.2
0.15
0.1
0.05
0
$k_2 (d^{-1})$
5.4
5.9
6.4
6.9
7.4
$\log K_{ow}$

Figure 1.4

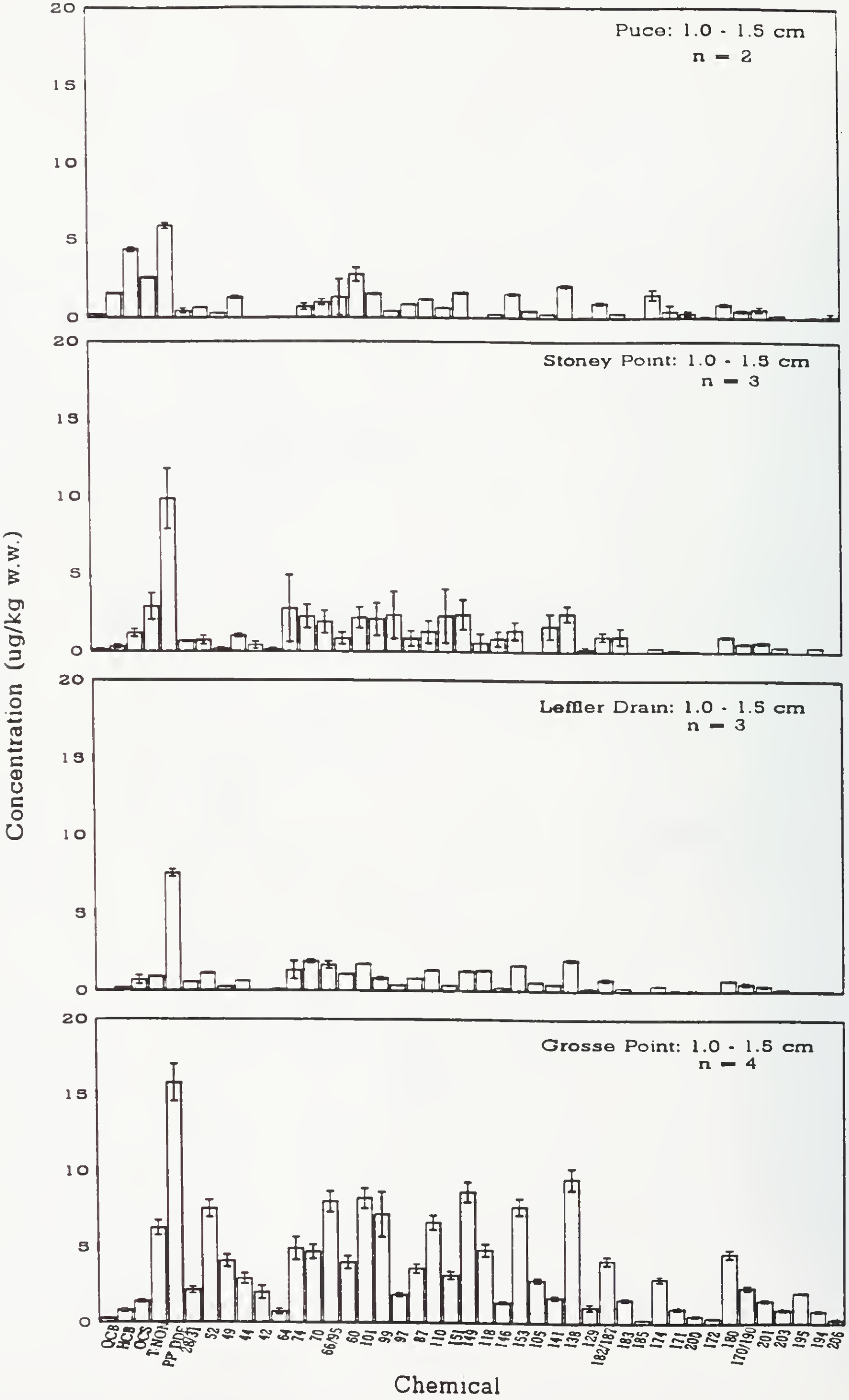

Puce: 1.0 - 1.5 cm
n = 2
Stoney Point: 1.0 - 1.5 cm
n = 3
Leffler Drain: 1.0 - 1.5 cm
n = 3
Grosse Point: 1.0 - 1.5 cm
n = 4
0
5
10
15
20
Concentration (ug/kg w.w.)
QCB
HCB
OCS
T.NON
PP DDE
28/31
52
49
44
42
64
74
70
66/95
60
101
99
97
87
110
151
149
118
146
153
105
141
138
129
182/187
183
185
174
171
200
172
180
170/190
201
203
195
194
206
Chemical

Figure 1.4 continued

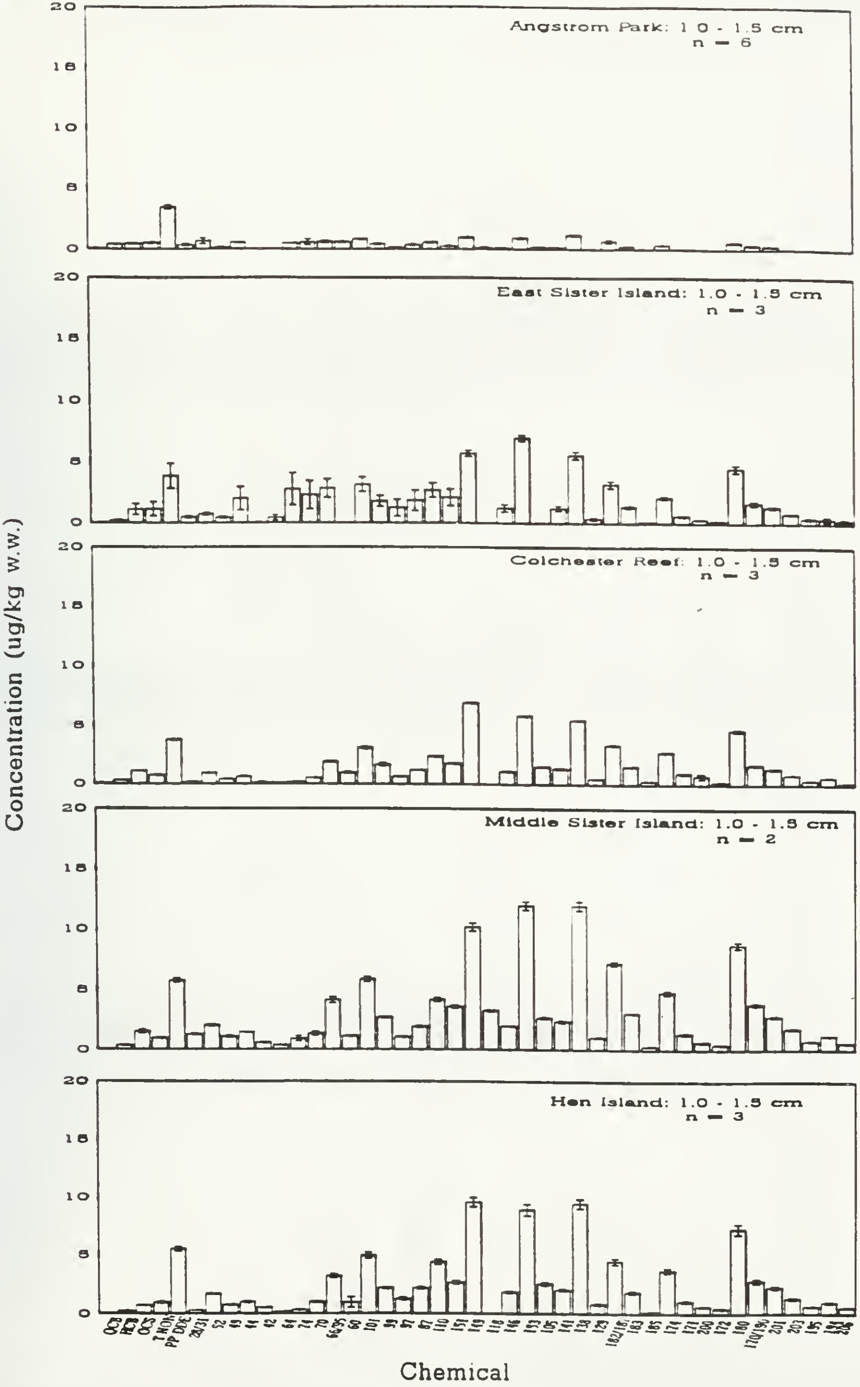


Figure 1.5

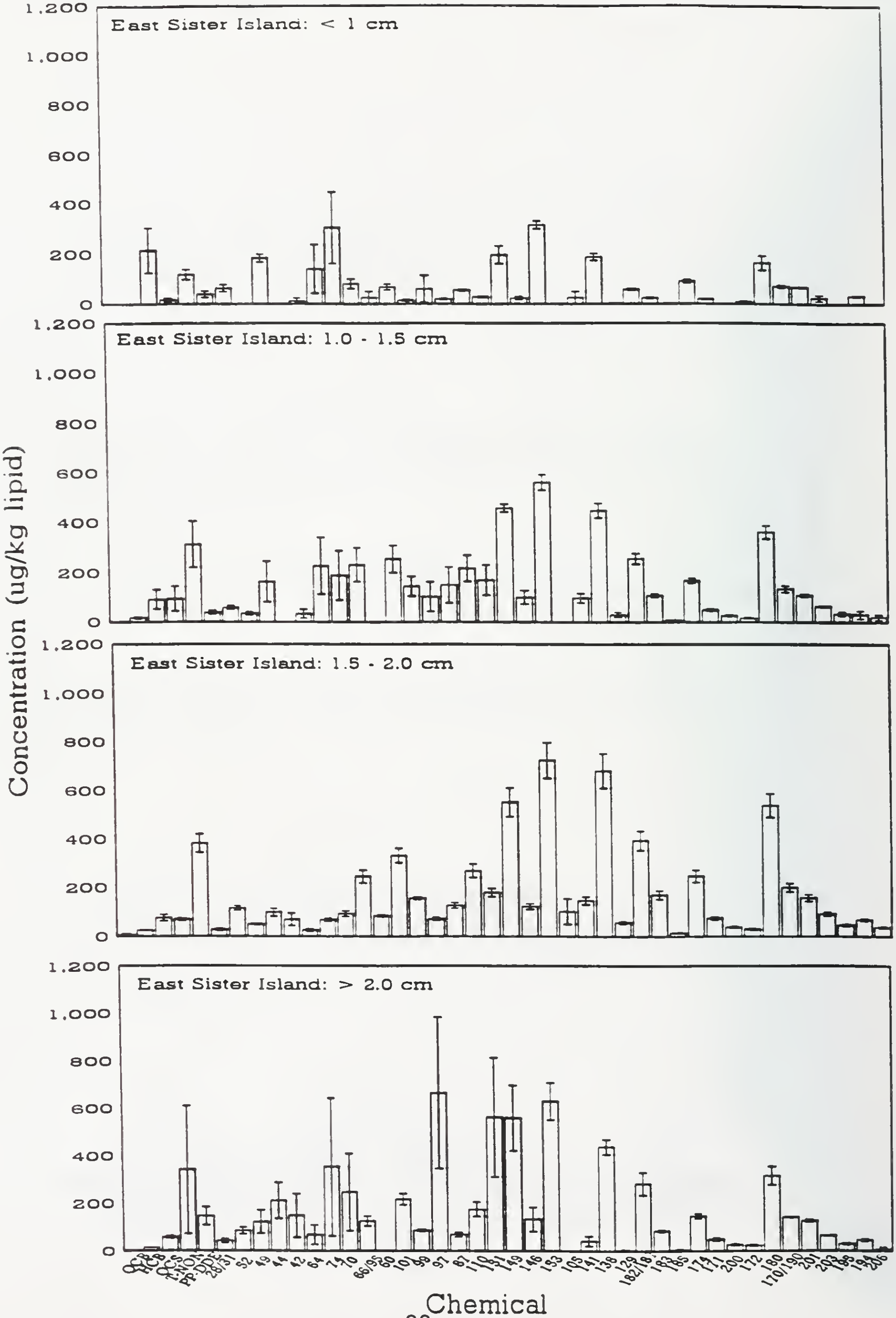

East Sister Island: < 1 cm
East Sister Island: 1.0 - 1.5 cm
East Sister Island: 1.5 - 2.0 cm
East Sister Island: > 2.0 cm
Concentration (ug/kg lipid)
0
200
400
600
800
1,000
1,200
Chemical
QCB
HCB
OCS
T.NON
PP-DDE
28/31
52
49
44
42
64
74
70
66/95
60
101
99
97
87
110
151
149
146
153
105
141
138
129
182/18
183
185
174
171
200
172
180
170/190
201
203
195
194
206

Figure 1.5 continued

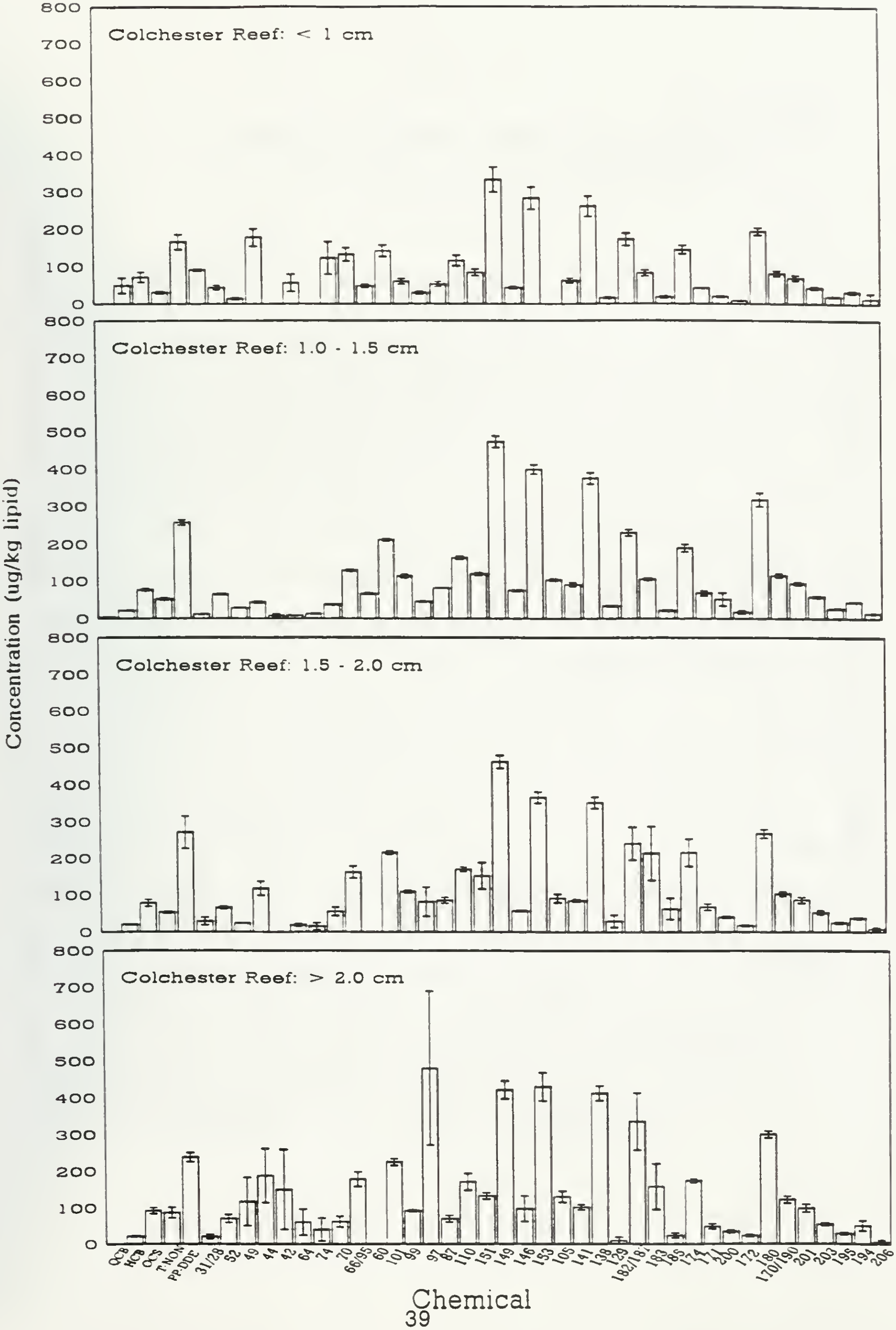
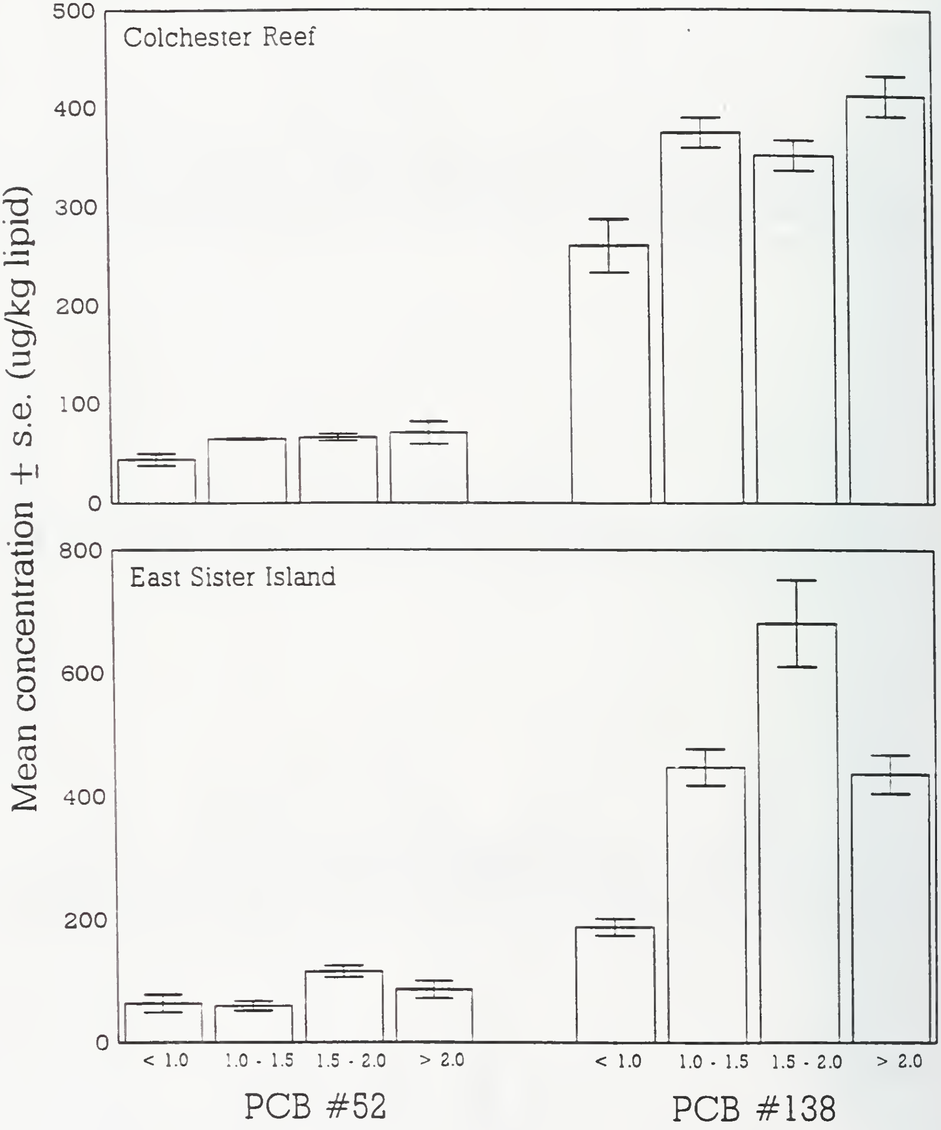


Figure 1.6



Mean concentration ± s.e. (ug/kg lipid)
Colchester Reef
500
400
300
200
100
0
East Sister Island
800
600
400
200
0
< 1.0
1.0 - 1.5
1.5 - 2.0
> 2.0
< 1.0
1.0 - 1.5
1.5 - 2.0
> 2.0
PCB #52
PCB #138

CHAPTER 2

Food Uptake of Ortho-substituted PCB congeners by the zebra mussel Dreissena polymorpha

Abstract

A laboratory experiment was performed to determine the contribution of food to zebra mussel PCB accumulation. Dry Chlorella powder was contaminated with the following ortho-substituted PCB congeners (IUPAC numbers): 4, 18, 28, 52, 101, 153, 138, 180, and 206. Mean concentrations in food varied from 9200 to 16940 ng g^{-1} lipid. Zebra mussels with very low background PCB levels were placed in 100-L aquaria (n=2). They were fed daily, for 16 d, with 5 mg dry weight of the contaminated powder (~1.5×10^4 algal cells mL^{-1}). The quantity of 'water-borne' contaminant accumulated by these mussels was determined by separating the treatment aquaria with 1.2-µm-porosity glass fibre membranes, which allowed passage of dissolved, colloidal and <1.2-µm-particulate-bound chemicals. Tissue concentrations of molluscs placed in algae-free compartments were used to correct for uptake of compounds not bound to algal cells. Temporal variations in zebra mussel lipid pool were minimized; percentage of lipids did not change significantly over time. Mussels accumulated low K_{OW} compounds more rapidly than high K_{OW} congeners. A linear negative relationship was detected between log of the uptake rate (ng contaminant/g tissue/d, estimated by linear regression) and the log K_{OW} for the congeners studied. We hypothesize that, for zebra mussels, water resistance in the gut controls organic contaminant assimilation from food, at least for compounds of log $K_{OW} \geq 4.5$.

Introduction

The assessment of the effects of anthropogenic contaminants in natural environments is part of the mandate of environmental protection agencies. The toxicity of these compounds to aquatic organisms depends upon the degree of exposure and potency. Therefore, predictions of contaminant toxicity require an understanding of the factors governing their bioaccumulation and their effects. In particular, knowledge of the rates of exchange of contaminants between an organism and its immediate environment may help to define the main routes of exposure of a given pollutant for any particular organism - e.g. water, food or sediment. This information, in turn, is necessary if one is to relate contaminant concentrations in organisms to bioavailable contaminant levels in the animal's environment. In addition, toxicokinetics are also important in the choice and the calibration of contaminant biomonitors in aquatic ecosystems. Information on dietary uptakes can be useful for the consideration of bioaccumulation through food chains in aquatic ecosystems.

Exchange rates, in nature, are poorly known. Laboratory studies dealing with uptake and depuration of pollutants are relatively recent too (metals: Hare et al. 1991; Riisgård et al. 1987; organic contaminants: benthic invertebrates: Landrum and Poore 1988; bivalves: Bruner et al. 1994a,b; Brieger and Hunter 1993; Russell and Gobas 1989; fish: Yamada et al. 1994; Gobas et al. 1989). The purpose of our laboratory study was to investigate the contribution of the dietary uptake to the bioaccumulation of ortho-substituted biphenyl congeners by the zebra mussel Dreissena polymorpha, an important epibenthic organism in the Great Lakes.

Uptake model

For an aquatic organism, the rate of uptake of an organic chemical from food and its depuration can often be described by the following differential equation (Gobas et al. 1988):

$$dC_{org}/dt = K_F C_F - K_E C_{org} - K_R C_{org} \qquad (1)$$

where C_{org} and C_F are contaminant concentrations the organism and its food, respectively, and K_F and K_E are uptake and elimination rate constants. K_R is the rate constant for metabolic transformation of the chemical in the organism. Implicit in this model are the following assumptions:

i) the lipid pool of the organism is the predominant reservoir for the organic contaminant;
ii) lipid levels within the organism remain constant over time; there is no growth;
iii) uptake and depuration rates remain constant over time;
iv) uptake and depuration kinetics can be described by first-order rate constants.

Molluscs have much lower activities of enzymes of the cytochrome P-450 and of the mixed-function oxidase systems than higher aquatic organisms. These enzymes are capable of metabolizing organic molecules (Walker 1987; Porte and Albaigès 1993). Also, because ortho-substituted PCBs have relatively low potencies to induce these enzyme systems (Safe et al. 1985), we have assumed that metabolic degradation in zebra mussels is negligible for the PCBs measured in this study. Thus, equation 1 simplifies to:

$$dC_{org}/dt = k_F C_F - K_E C_{org} \qquad (2)$$

In this study, organisms were exposed to contaminated food but uncontaminated water. Characteristics of the methodology used to satisfy the above-mentioned assumptions of the uptake model are discussed below.

Materials and Methods

Organisms

Approximately 40,000 Dreissena with very low PCB burdens (Table 2.1) were collected by hand in early September 1994 from Tremblay Beach, L. St. Clair. Small clumps of animals were collected by hand from a region of sandy bottom between macrophyte stands 200-300 m offshore at a depth of 1.5 m. Water temperature was 21°C. Six animals, examined under a dissecting microscope, were nongravid. The condition index of a composite sample of 30 animals (C.I.: total dry weight of soft tissue/total shell weight) was 0.034 (mean shell length 21.6 mm).

In the laboratory, the animals were kept at room temperature (19-22°C) in three 160-L glass aquaria filled with dechlorinated City of Windsor tap water. They were fed 3.5 g dry, uncontaminated (Table 2.1) Chlorella powder every other day. Water, was continuously aerated with air pumps and filtered over activated carbon and ammonia chips to remove ammonia and chemicals eliminated by the mussels. Water was replaced weekly. Water temperature, oxygen concentration and ammonia concentration measured on three occasions averaged 24°C, 6.1 mg/L and 0.1 mg/L, respectively. The mussels remained in a stable condition until the beginning of the experiment approximately 2 mo. later.

Contaminants

Nine ortho-substituted PCB congeners, ranging in K_{OW} from 4.65 to 8.09 were purchased from Chromatographic Specialties, Inc. (35 mg PCB mL^{-1} isooctane solution). Their characteristics are summarized in Table 2.2.

Preparation of contaminated food

In a clean, 2.8-L, foil-covered glass flask, 6,000 ng (171 mL of isooctane solution) of each of the 9 PCB congeners, together with 20 g of dry Chlorella powder were incorporated in 2 L of hexane ('Omnisolv' grade). The flask was covered with clean aluminum foil and an elastic band. In order to keep the material in suspension, the mixture was shaken continuously on a wrist-action shaker (130 rpm) for 6 h at room temperature. The flask was then uncovered, and the hexane allowed to evaporate under a fume hood. At the end of the 6-h shaking period, the hexane was very slightly green; 19.75 g of contaminated powder was recovered . Mean concentrations in food varied from 109 to 200 ng g^{-1} dry weight; mean lipid was 1.2% (n=4). Mean lipid-corrected contaminant levels in the food are listed in Table 2.2.

Design of the experimental aquariums

Contaminated food given to the mussels was kept in suspension in 100-L aquaria with underwater filters. We expected that food-bound contaminants coming into contact with uncontaminated water would partition between food, the dissolved phase (water) and other uncontaminated particles, because of unequal fugacities between these compartments. In order to ascertain the amounts of PCBs accumulated by the mussels from water-only vs. water+food+other particles, we separated the two halves of treatment aquaria with 1.2 µm-porosity glass fibre membranes (Gelman Co.). The membranes allowed diffusion of dissolved, colloidal and <1.2 µm-particulate-bound chemicals (hereafter referred to as waterborne chemicals) throughout aquaria, but restricted larger particles to the treatment side of an aquarium. Ninety-eight percent of single algal cells (food particles) were 1.7 - 5 µm in diameter. The remaining 2% of material consisted of 4-cell aggregates 7-9 µm in diameter. Tissue concentrations of unfed mussels placed in these algae-free compartments were to be used to correct for uptake of desorbed, water-borne compounds.

Behaviour of three reference aquaria was studied using algal cell suspensions in the absence of zebra mussels. Eight-mL water samples were withdrawn from points 10 cm from the bottom , middle (1-h intervals for 3 h), and 10 cm from the top of each tank. Samples were transferred to sedimentation chambers, and after 24 h cells settling to the bottom were counted using an inverted microscope at 400X magnification. Algal cell suspensions were homogeneously distributed in the aquaria (ANOVA; F(2:6)=1.58, $P>0.05$) and cell numbers did not decline over time (ANOVA: F(3:8)=0.48, $P>0.05$). Thus, sedimentation and cell trapping by the membranes were unimportant processes in the experimental aquaria. Red dye injected into water on one side of the aquarium did not readily diffuse to the other side, suggesting that the membranes were relatively impermeable to dissolved material. Hand-transferring 1.3X the volume on one side of the aquarium to the other resulted in an homogeneous distribution of the dye all over the aquarium.

Two hundred mussels were introduced into one side of each of three aquaria along with food suspensions (~2×10^4 cells mL^{-1}). Most cells had been consumed within 6.5 h. 1.3X the volume of the unfed sides was then transferred to the fed sides and the remaining cells in suspension were captured by membranes. Considering the behaviour of the systems, it was deemed appropriate to perform water exchanges 6.5 h after daily feeding in the uptake experiment.

Uptake experiment

Two hundred zebra mussels, (length 18-22 mm), were introduced into the 'food-present' side of each of 2 100-L aquaria filled with 0.7 µm-filtered water from Tremblay Beach, Lake St. Clair. One hundred and sixty molluscs were placed in the algae-free compartment. Animals on the food-present side were fed 5 mg dry weight contaminated food (~1.5×10^4 algal cells mL^{-1}) daily for 16 d. Eight-mL water samples were withdrawn from the middle of the water column on each fed side of each aquarium 0, 1, 2, 4, 6, 8, 10, 12, and 14 d after the start of the experiment. Samples were taken immediately after feeding, 6.5 h after food addition, immediately after water transfer, and 24 h later. These samples were used to estimate the day-to-day variation in food consumption. The tissue concentrations of unfed mussels were used to correct for uptake of desorbed, water-borne compounds. Unfed animals were received no algae for the 16-d duration of the experiment.

Zebra mussel pumping rates have a substantial effect on kinetics of uptake and depuration of organic contaminants in filter-feeders (Farrington 1975). Preliminary tests (unpubl. obs.) showed that pumping rates of fed and unfed mussels were not significantly different for 72 h, at room temperature, at the algal densities used in the present experiment (n=5; 0.5 mg dry Chlorella/4.5 L/d for 20 mm-long mussels; ANOVA on adjusted means; F(1:250)=0.445, P>0.05). This condition was a prerequisite for the above-mentioned correction. Two control aquaria containing fed mussels and two control aquaria containing unfed mussels accounted for extraneous sources of PCBs and internal recycling of PCBs.

All aquaria were held in an environmental chamber at 17°C and with a 12 h light : 12 h dark photoperiod. They were covered with aluminum foil to minimize evaporation, aerial particle deposition, and light. Mortality was recorded every day and water temperature, O_2 and NH_3 levels were measured every other day in all the tanks. In order to minimize stress, all mussels were left attached to their original clumps. To minimize ingestion of feces, mussels were placed on metal grids (0.5 cm mesh size) suspended in the middle of the water column.

Twenty-25 fed and unfed mussels from each treatment tank were removed 0, 1, 2, 4, 8, 12, and 16 d after the experiment began. Unfed mussels were harvested 6.5 h later than fed mussels. The animals collected were immediately replaced by an equal number of mussels, marked, and of a similar size. Control aquaria were sampled after 16 d only. The groups of mussels removed were frozen and stored at -20°C prior to preparation for chemical analysis, 1 to 2 weeks later. For the chemical extractions, the mussel groups were partially thawed and the mussels individually measured, weighed, shocked (the byssal threads and the internal liquids were not retained). In all, 604 mussels measuring 20.0 ± 5.1 mm (mean ± SD) were prepared. The mussel groups were pooled to provide a composite sample for PCB congener-specific analysis. The condition index (C.I.) {Total dry weight of soft tissues/total shell weight} was determined on from the composite samples of 0 and 16 d.

Chemical analyses

The protocol for chemical analyses is described in chapter 1. Reference standard material was analyzed every 5 samples (CWS- RSM 8229 - Herring gull Egg pool-Dil 9:1(A)); values measured were within the certified ranges for PCB congeners of this study. Three experimental samples were run as unknowns. Recoveries of standard solutions were >90% except for PCB 4 for which recovery was somewhat less (67% and 81% for two runs, respectively).

All aquaria, environmental chambers and labware were precleaned with acetone, petroleum ether and hexane to minimize organic contamination.

Statistical analyses

Concentrations of chemicals in mussels exposed to contaminated food were corrected for initial (t=0) and water-borne concentrations (obtained from the non-fed mussels). Changes of these concentrations over time were initially summarized by plotting bivariate scatter diagrams. The BIOFIT model, a non-linear regression model based on iterative numerical integration (Gobas and Zhang 1992) was used to calculate kinetic rate constants. Linear regressions were also used to describe the relationships between contaminant levels and time. Results are discussed below.

Results

Environmental conditions

Environmental conditions during the experiment were relatively constant. Thus, assumptions of the uptake model were largely met.

Lipid levels in the mussels in the experimental treatments remained constant over time (ANOVA: F(6:20)=1.45; P>0.05; ranges of lipid 0.87-1.47%). Ammonia concentrations remained low (mean±SE = 0.34±0.2 mg L^{-1}, n=43). Oxygen saturation was high throughout the experiment (mean±SE = 0.91±0.01, n=43). Water temperature was also constant at 17.58±0.05°C, n=43. Condition indices obtained from the pooled samples of the experimental treatments were similar at the beginning and at the end of the experiment (0 d: 0.046±0.003, n=3; 16 d: 0.042 ± 0.004, n=3). Cumulative mortality of unfed mussels reached 18% after 16 d. In contrast, C.I. and cumulative mortality for the fed controls at 16 d were 0.020±0.003, n=2; 37%. C.I. and cumulative mortality for the non-fed controls at 16 d were 024±0.002 n=2 and 50%, respectively.

The exposure levels used in this experiment were environmentally realistic (in the range of normal field exposure concentrations). Algal densities were typical of the plankton densities in the western basin of Lake Erie during summer. Chemical levels, although somewhat higher for some congeners, were within the same order of magnitude as the concentrations found in the plankton of this basin for some congeners (Table 2.3).

Uptake

With the exception of congeners PCB 52 and 206, mussels exposed to contaminated food significantly bioaccumulated chemicals over time (Figure 2.1). PCB 206 was not detected in any of the samples analyzed, whereas PCB 52 was. Control mussels also accumulated significant amounts of the PCBs over time. These chemicals most probably evaporated from treatment tanks and entered the control uncontaminated tanks by aerial transport and deposition. PCB levels measured in control animals corresponded closely with vapour pressures of the different PCB congeners (Table 2.4).

The BIOFIT model, a non-linear regression procedure, was applied to the data (mean values) to generate rate constant estimates and permit calculation of biomagnification factors. This program is designed to provide estimates in cases where test duration was too short to reach steady state (see Figure 2.1) and exposure levels vary over time (Gobas and Zhang 1992). In our experiment, quantities of algal cells eaten by the exposed molluscs (i.e. the exposure levels) varied from day to day.

The goodness-of-fit, i.e., the mean deviation between experimental and fitted concentration data ranged from 20-35% for congeners 101, 153, 138 and 180. Mean deviations for the low K_{OW} congeners (4, 18, 28) were larger, with a range of 44-50%. Fitted and experimental concentrations were in better agreement for the congener 52 even though this congener was not accumulated to a significant extent over time (Figure 2.1).

Biomagnification factors (defined as k_F/k_E) appeared to be erroneous for all the congeners. We concluded that the data were inadequate to be described by non-linear regressions because observations were not taken over a sufficient time period for steady-state conditions to be achieved.

Linear regressions better described the relationships between mean contaminant levels in exposed mussels and time: coefficients of determination (R^2) for linear regressions ranged from 58-79% (Fig. 2.1, Table 2.2). The slope was not significantly different from zero for PCB 52.

The 12-d data point was excluded from regression analyses for the congeners 101, 138, and 153. Algal consumption from 8-12 d averaged 3.6 and 8.0 mg, respectively, for all mussels in each treatment. Whereas tissue levels increased for most of the congeners at that time, those for the above chemicals were inexplicably low. These data points were subsequently identified as statistical outliers (Dixon's test, α=0.05; Dunn and Clark 1974).

Discussion

Increases in tissue contaminant levels over time for mussels exposed to contaminated food were best explained by linear regression relationships for the low K_{OW} PCB congeners 4, 18 and 28. Contaminant uptake of high K_{OW} compounds (PCBs 101,153,138,180) was explained equally well by linear and non-linear regression procedures. If we assume that at the end of the study, mussels were far from steady-state for any of the contaminants tested (Fig. 2.1), then the term $k_E C_{org}$ in equation 2 can be considered small relative to the term $k_F C_F$ in the course of the present exposure. The slopes of the linear regressions presented in Table 2.2 can then be considered approximate representations of the uptake rates k_F. These slopes are hereafter defined as K_a.

There is a significant negative linear relationship between $\log(K_a+1)$ and $\log K_{OW}$ of the different congeners studied in this experiment (Figure 2.2, $P< 0.01$). K_as of PCB 52 and 206 are not considered in the relationship since it is unlikely that they represent the true relationship between uptake and the hydrophobicity for these two compounds (If they are included, the relationship is still negative with $r = -0.81$, $P<0.01$).

An explanation to the above result may be found in the model of the mechanics of contaminant absorption proposed by Gobas et al. (1993). As the algal particles move down the digestive tract, cell membranes are broken down in the presence of enzymes, and chemical components such as fatty and amino acids are assimilated. The reduction in food volume as a result of digestion results in an increase of the chemicals' fugacity in the food; this provides the driving force for the hydrophobic chemical to be assimilated (Gobas et al. 1993). In the present case, it is possible that this driving force (fugacity) is efficiently counteracted by the resistance to assimilation provided by the aqueous diffusion layers located between food and organism lipid reservoirs. This suggests that, in the case of the zebra mussel, water resistance in the gut controls organic contaminant assimilation from food, at least for compounds of log $K_{OW} \geq 4.5$.

Support for the above explanation is provided by the work of Bruner et al. (1994b). The reduction of the chemical's capacity of the food (caused by digestion) together with increased water resistance to assimilation with increasing hydrophobicity of the compound should result in

i) increased concentrations of hydrophobic chemicals in the feces compared with that in food items ingested;

ii) increases that are relatively larger for higher K_{OW} compounds.

Bruner et al. (1994b) studied 2-h exposures of zebra mussels to cells of Chlamydomonas reinhardii contaminated with 2,2',4,4'-tetrachlorobiphenyl and 2,2',4,4',5,5'-hexachlorobiphenyl. Feces produced during the experiment were collected and assayed for these compounds. Concentrations of tetra-PCB in the algal cells and in the feces were 91 ng g^{-1} wet weight and 12 $\mu g\ g^{-1}$ wet weight, respectively; concentrations of hexa-PCB in the food and in the feces were 210 ng g^{-1} wet weight and 36 $\mu g\ g^{-1}$ wet weight, respectively. Ratios of the concentration in the feces over that in the food was larger for the hexa-PCB (171), than that for the tetra-PCB, (132).

References

Brieger, G., and R.D. Hunter. 1993. Uptake and depuration of PCB 77, PCB 169, and hexachlorobenzene by zebra mussels (Dreissena polymorpha). Ecotox. Environ. Safety 26: 153-165.

Bruner, K.A., S.W Fisher, and P.F. Landrum. 1994a. The role of the zebra mussel, Dreissena polymorpha, in contaminant cycling: I. The effect of body size and lipid content on the bioconcentration of PCBs and PAHs. J. Great Lakes Res. 20: 725-734.

Bruner, K.A., S.W Fisher, and P.F. Landrum. 1994b. The role of the zebra mussel, Dreissena polymorpha, in contaminant cycling: II. Zebra mussel contaminant accumulation from algae and suspended particles, and transfer to the benthic invertebrate, Gammarus fasciatus. J. Great Lakes Res. 20: 735-750.

Dunn, O.J. and V.A. Clark. 1974. Applied Statistics. Analysis of variance and regression. Wiley and Sons, Toronto.

Farrington, J. 1975. Bioaccumulation of hydrophobic organic pollutants. In F. Moriarty (ed.). Organochlorine insecticides: persistent organic pollutants. Academic Press. London.

Gobas, F.A.P.C., K.E. Clark, W.Y. Shiu, and D. Mackay. 1989. Bioconcentration of polybrominated benzenes and biphenyls and related superhydrophobic chemicals in fish: role of bioavailability and elimination in the feces. Environ. Toxicol. Chem. 8: 231-245.

Gobas, F.A.P.C., J.R. McCorquodale, and G.D. Haffner. 1993. Intestinal absorption and biomagnification of organochlorines. Environ. Toxicol. Chem. 12: 567-576.

Gobas, F.A.P.C., R.W. Russell, and G.D. Haffner. 1988. Biomonitoring: chemical dependent quantitative relationships for the body burdens of organic chemicals in aquatic organisms. In: Proc. Technol. Transfer Conf. OMOE. Toronto. ISSN 0840-8440.

Gobas, F.A.P.C., and X. Zhang. 1992. Measuring bioconcentration factors and rate constants of chemicals in aquatic organisms under conditions of variable water concentrations and short exposure time. Chemosphere 25: 1961-1971.

Hare, L., E. Saouter, P.G.C. Campbell, A. Tessier, F. Ribeyre, and A. Boudou. 1991. Dynamics of cadmium, lead, and zinc exchange between nymphs of the burrowing mayfly Hexagenia rigida (Ephemeroptera) and the environment. Can. J. Fish. Aquat. Sci. 48: 39-47.

Hawker, D.W., and D.W. Connell. 1988. Octanol-water partition coefficients of polychlorinated biphenyl congeners. Environ. Sci. Technol. 22: 382-387.

Landrum, P.F., and R. Poore. 1988. Toxicokinetics of selected xenobiotics in Hexagenia rigida. J. Great Lakes Res. 14: 427-437.

Porte, C., and J. Albaigés. 1993. Bioaccumulation patterns of hydrocarbons and polychlorinated biphenyls in bivalves, crustaceans, and fishes. Arch. Environ. Contam. Toxicol. 26: 273-281.

Riisgård, H.U., E. Bjørnestad, and F.Møhlenberg. 1987. Accumulation of cadmium in the mussel Mytilus edulis: kinetics and importance of uptake via food and sea water. Mar. Biol. 96: 349-353.

Russell, R.W., and F.A.P.C. Gobas. 1989. Calibration of the freshwater mussel, Elliptio complanata, for quantitative biomonitoring of hexachlorobenzene and octachlorostyrene in aquatic systems. Bull. Environ. Contam. Toxicol. 43: 576-582.

Safe, S., S. Bandiera, T. Sawyer, L. Robertson, L.Safe, A. Parkinson, P.E. Thomas, D.E. Ryan, L.M. Reik, W. Levin, M.A. Denomme, and T. Fujita. 1985. PCBs: stucture-function relationships and mechanism of action. Environ. Health. Perspect. 60: 47-56.

Walker. C.H. 1987. Kinetic models for predicting bioaccumulation of pollutants in ecosystems. Environ. Pollut. 44: 227-240.

Yamada, H., M. Tateishi, and K, Takayanagi. 1994. Bioaccumulation of organic compounds in the red sea bream (Pagus major) by two uptake pathways: dietary uptake and direct uptake from water. Environ. Toxicol Chem. 13: 1415-1422.

Table 2.1. Concentrations of PCB congeners in zebra mussels collected at Tremblay Beach, L. St. Clair and in the food used to feed them in captivity.

	Congener concentrations (ng g^{-1} wet wt)						
	28	52	101	138	153	180	206
Zebra mussel	0.14	0.28	0.28	0.48	0.44	0.29	N.D.
Dry *Chlorella* powder	N.D.[a]	N.D.	N.D.	0.07	N.D.	N.D.	N.D.

[a] Non detected

Table 2.2. Characteristics of the PCB congeners used in this study, slopes(K_a), intercepts, and explained variances for the linear regressions between mean PCB tissue levels [a] vs time for the mussels exposed to contaminated food, and contaminant concentrations in the food.

Congener no	Substitution pattern	Log K_{OW} [b]	K_a (ng g^{-1} d^{-1})	Intercept	R^2	C_{food} (ng g^{-1} lipid)
4	2,2'	4.65	178.958	-244.898	0.77	9200
18	2,2',5	5.24	34.710	54.097	0.58	10420
28	2,4,4'	5.67	62.372	47.743	0.79	12790
52	2,2',5,5'	5.84	0	75.670	0.06	13880
101	2,2',4,5,5'	6.38	0.637	1.859	0.75	14280
138	2,2',3,4,4',5'	6.83	0.610	0.537	0.79	15990
153	2,2',4,4',5,5'	6.92	0.786	1.479	0.72	14580
180	2,2',3,4,4',5,5'	7.36	0.361	0.775	0.74	16940
206	2,2',3,3',4,4',5,5',6	8.09	0	---	---	16940

[a] Tissue concentrations corrected for initial and water-borne concentrations, and expressed on a lipid basis.

[b] Values taken from Hawker and Connell (1988).

Table 2.3. Contaminant levels and densities of plankton[a] at some locations in the western basin of Lake Erie compared with that in our study.

Location	Plankton density	PCB congener concentrations (ng g^{-1} lipid)								
	(mg dry wt L^{-1})	4	18	28	52	101	138	153	180	206
Middle Sister Is.	0.02-0.24	ND	61	ND	320	470	400	541	358	17
Mouth of Detroit R.	0.034	ND	415	178	1218	1621	2337	1816	1151	19
This study	0.050	9200	10420	12790	13880	14280	15990	14580	16940	16940

[a] Plankton samples were obtained from vertical tows of a plankton net with a mesh size of 50 µm. Densities were determined from the volume of water sampled and the estimated dry wt of the plankton items collected by the tow.

Table 2.4. Accumulation of contaminants by fed and unfed control zebra mussels at the conclusion of the experiment. Mean concentrations (n=2) are corrected for initial levels (t=0) of PCBs[a].

	PCB congeners concentrations (ng g^{-1} lipid; mean± SD)							
Control mussels	4	18	28	52	101	153	138	180
Unfed	4330 ± 4990	4195 ± 250	1590 ± 7	460 ± 80	98 ± 110	130 ± 120	140 ± 100	45 ± 60
Fed	6890 ± 75	5340 ± 350	2090 ± 2	570 ± 2	22 ± 8	29 ± 24	16 ± 10	16 ± 23
Vapor P (Pa)	$10^{-0.538}$	$10^{-0.939}$	$10^{-1.620}$	$10^{-1.524}$	$10^{-2.62}$	$10^{-3.102}$	$10^{-3.367}$	$10^{-3.866}$

[a] PCB 206 was not accumulated; its vapor pressure is $10^{-4.721}$

Figure Legends

Figure 2.1. Scatter diagrams of PCB congener concentrations in mussels exposed to contaminated food vs. time. Regression lines are indicated; coefficients and percentage explained variance are found in Table 2.2. For PCBs # 101, 153 and 138 the data points at 12 d were not included in the regressions (see text).

Figure 2.2. Scatter diagram of log (K_a+1) vs. log K_{OW} for the congeners used in this study. Congeners # 52 and 206 are not included in the relationship shown (see text). K_{as} represents the slope of the regressions between PCB tissue levels in exposed mussels and time; as such, it is an approximation of the actual uptake rate (see text).

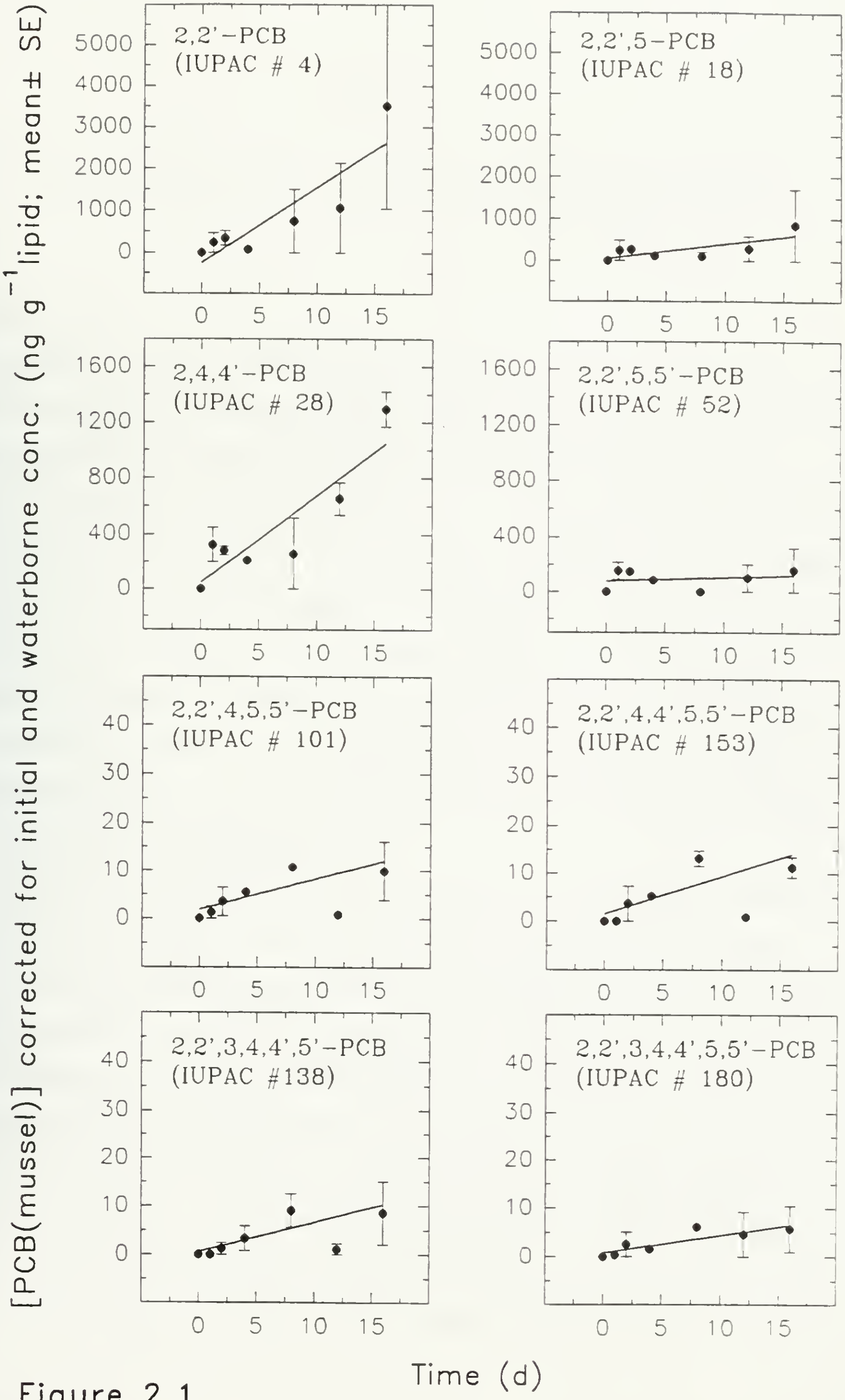
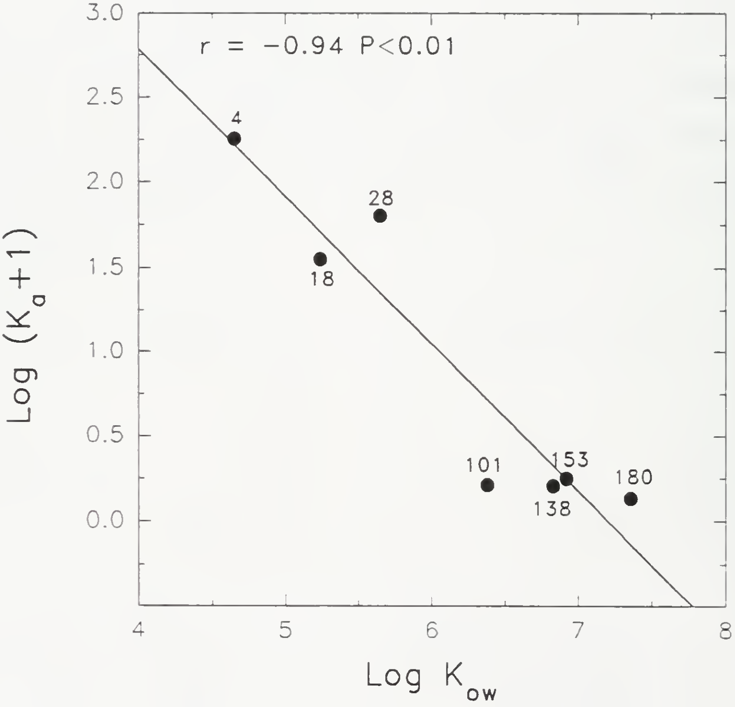

[PCB(mussel)] corrected for initial and waterborne conc. (ng g^{-1} lipid; mean± SE)
2,2'-PCB (IUPAC # 4)
2,2',5-PCB (IUPAC # 18)
2,4,4'-PCB (IUPAC # 28)
2,2',5,5'-PCB (IUPAC # 52)
2,2',4,5,5'-PCB (IUPAC # 101)
2,2',4,4',5,5'-PCB (IUPAC # 153)
2,2',3,4,4',5'-PCB (IUPAC #138)
2,2',3,4,4',5,5'-PCB (IUPAC # 180)
0
1000
2000
3000
4000
5000
400
800
1200
1600
10
20
30
40
5
15
Time (d)

Figure 2.1



3.0
2.5
2.0
1.5
1.0
0.5
0.0
Log $(K_a + 1)$
$r = -0.94$ $P<0.01$
4
28
18
101
153
138
180
4
5
6
7
8
Log K_{ow}

Figure 2.2

CHAPTER 3

Organic contaminant profiles of lower Great Lakes' waterfowl in relation to diet, with particular reference to Dreissena polymorpha

Abstract

Six species of waterfowl (greater and lesser scaup, bufflehead, canvasback, mallard, redhead) were collected from sites in the lower Great Lakes (Fighting Island, western Lake Erie, Big Creek) and analyzed for diet contents and for profiles of organic contaminants. Lesser and greater scaup from Fighting Island were classified into groups according to the percentage dry mass of zebra mussel in the diet. Lesser and greater scaup classified as Dreissena-consumers had, on average, 85 and 67%, respectively, zebra mussel diet content as compared to 6 and 3% for individuals classified as Dreissena non-consumers. Other taxa consumed little (8%; bufflehead) or no (canvasback, mallard , redhead) Dreissena at the Fighting Island location. Dreissena was the primary food source of lesser scaup (100%), greater scaup (97%) and bufflehead (67%) in western Lake Erie.

A selection of low- (QCB, PCB #28), mid- (PCBs #149, 153) and high- (PCBs #194, 206) K_{OW} compounds were examined in liver tissues for each group of waterfowl. Two-way ANOVAs on log-tranformed, lipid-adjusted contaminant values for greater and lesser scaup from Fighting Island failed to reveal significant differences among species, though differences with respect to diet for mid- (PCB #153) and high-K_{OW} (PCBs #194, 206) compounds were significant ($p \leq 0.05$). In each case, mussel consumers had elevated concentrations of these compounds relative to individuals that avoided Dreissena. Two-way ANOVAs were also used to assess differences among Dreissena-consuming species at the two major sites. All six compounds were present in significantly ($p<0.05$) higher concentrations in lake individuals; however,

differences among species were insignificant ($p > 0.05$). Bufflehead from Lake Erie had significantly higher concentrations of the mid- and high-K_{OW} compounds than individuals from Fighting Island, though the greater prevalence of Dreissena in lake individuals confounds this difference. Differences in concentrations of all six compounds in mallard from Fighting Island and Big Creek were minor and insignificant ($p > 0.10$). Concentrations of each compound in Fighting Island canvasback and redhead were similar to those in mallard at that site (<100 µg/kg lipid).

Principal component analysis was conducted for duck livers using the six chemicals described above plus two additional low (hexachlorobenzene, octachlorostyrene), mid- (PCB # 105, 118) and high- (PCB # 180, 174) K_{OW} compounds. PC 1 accounted for 44% of the original data variability, and was determined primarily by high K_{OW} compounds (PCB # 206, 153, 194, 180, 118, 105). Compounds used PC 2 and PC 3 accounted for additional 19% and 18% of data variability and were respectively determined by low K_{OW} (HCB, QCB) or mid K_{OW} (PCBs # 149, 174) compounds. Waterfowl that consumed mainly Dreissena separated clearly on PC 1 and/or PC2 from ducks that avoided Dreissena. Fighting Island greater and lesser scaup that consumed mussels were in between Lake Erie mussel-consumers and Fighting Island macrophyte-consumers. PC1 scores for mussel-consuming scaup did not vary by species or by site. PC 2 scores of mussel-consuming lesser and greater scaup differed marginally ($p=0.068$) by site, though differences between species were not evident. Fighting Island scaup PC1 scores differed significantly ($p<0.05$) by diet (mussel vs. macrophyte consumers) but not by species ($p>0.10$).

Biomagnification factors (BMFs), calculated for 40 organic compounds for mussel consumer scaup using Dreissena from Middle Sister Island as a reference, were generally below five though values for dieldrin, octachlorostyrene, mirex, and PCBs

#195 and 206 ranged between 7.5 and 25.3 in greater scaup. BMFs in lesser scaup tended to be lower than those in greater scaup. BMFs increased slightly with increasing $\log K_{OW}$ above ~5.8.

Results from this study indicate that concentrations of most contaminants are biomagnified in waterfowl that consume D. polymorpha as a primary food source. Consequently, zebra mussels may serve as both an energy source and conduit for transfer of persistent organic contaminants to higher trophic levels in the Great Lakes. However, it is not clear whether consumption of Dreissena portends adverse reproductive effects in Great Lakes waterfowl.

Introduction

Zebra mussels are now dominant contributors to benthic biomass in numerous Great Lakes ecosystems, including western and central Lake Erie, Lake St. Clair and Saginaw Bay (Leach 1992; Mackie 1991; Griffiths 1992; Nicholls and Hopkins 1993; Holland 1993; Nalepa 1994). Well-established effects of Dreissena include enhanced water transparency, reduced turbidity and reduced abundances of phytoplankton, zooplankton, and unionid molluscs (MacIsaac, in review). Less well known are effects of predators on Dreissena abundance, size structure, and role in contaminant dynamics.

Recent studies have described predation of Dreissena by a host of taxa including crayfish (MacIsaac 1994), fishes (French 1993) and waterfowl (Wormington and Leach 1992; Hamilton et al. 1994). Waterfowl appear the most likely candidates to have a significant impact on Dreissena populations both in North America (Hamilton et al. 1994) and in Europe (Stempniewicz 1974; Stanczykowska et al. 1990; Bij de Vaate 1991; Cleven and Frenzel 1993). The most common waterfowl associated with Dreissena predation on Lake Erie are greater scaup Aythya marila, lesser scaup A. affinis, common goldeneye Bucephala clangula and bufflehead B. albeola

(Wormington and Leach 1992; Hamilton et al. 1994). Wormington and Leach (1992) recorded dramatic increases in the number of staging greater and lesser scaup and common goldeneye subsequent to *Dreissena* establishment in the west basin. Moreover, the duration of stay of staging ducks appears to have lengthened subsequent to *Dreissena* establishment (Wormington and Leach 1992). During their stay in the Lake Erie area, ducks may have significant effects on *Dreissena*. For example, Hamilton et al. (1994) determined that waterfowl staging during autumn in the Point Pelee, ON, area of western Lake Erie consumed 57% of *Dreissena* biomass in nearshore waters. In addition, waterfowl have been reported drowned in commercial gill nets deployed in western Lake Erie in regions known to support *Dreissena* (E. Mazak, unpubl. data).

Recent studies have demonstrated the utility of *D. polymorpha* as a biomonitor of metal (e.g. Secor et al. 1993; Mersch et al. 1993; Kraak et al. 1994) and organic (e.g. Duursma et al. 1984; Fisher et al. 1992; Doherty et al. 1993; Brieger and Hunter 1993; Marvin et al. 1994; chapters 1 and 2) contamination. The species appears particularly well suited as a biomonitor owing to its rapidly increasing North American distribution, large population sizes, and ability to concentrate PCBs to a greater extent than native taxa (see chapter 1). For example, Brieger and Hunter (1993) reported that zebra mussels from Lake St. Clair and Lake Erie had higher accumulations of Aroclors 1242 and 1254 than did native *Lampsilis siliquoidea* clams. Additional details describing the utility of and limits to employing *Dreissena* as a biomonitor are reported in earlier chapters.

Little information exists regarding potential biomagnification of organic contaminants in predators that feed extensively on *Dreissena*. However, de Kock and Bowmer (1992) found that European tufted ducks (*Aythya fuliga*) fed zebra mussels contaminated with a wide array of organic compounds (PCBs, DDE, HCB) laid fewer eggs, abandoned nests more often and had higher embryo and chick mortality rates than ducks fed less polluted mussels. The purpose of this study was to determine whether waterfowl frequenting the lower Detroit River and western Lake Erie differ with respect to contaminant concentrations and profiles based on waterfowl species, diet or location, and whether biomagnification occurs in ducks that consume Dreissena.

Methods

Collection Site Descriptions

Waterfowl were collected from two major sites, Fighting Island in the lower Detroit River, and in western Lake Erie between Middle Sister and Hen Islands and the north shore. Historically, Fighting Island was a dumping site for Wyandotte Chemical (Michigan). A wetland downstream of Fighting Island is used extensively by migrating and local waterfowl (E. Mazak, pers. obs.). Hunting is prohibited in the wetland, which serves as a sanctuary. Nearby shallow areas within the river are rich in aquatic macrophytes such as Vallisneria americana, Elodea canadensis and Potamogeton spp. Gastropods and Dreissena occur on macrophytes and on mudflats in the area (E. Mazak, pers. obs.).

Hen Island is located 8 km west of Pelee Island in western Lake Erie. Middle Sister Island is located west of Hen Island, 15.7 km from the Canadian mainland (Colchester, ON) in the central region of western Lake Erie. Water between these islands and the Canadian mainland reaches 13 m maximum depth. Commercial fishermen employ gill nets extensively throughout the western basin of the lake, including in the study area.

Duck Collection

125 waterfowl were collected in total. Individuals from Fighting Island were donated by duck hunters from LaSalle Sportsmen's Club who agreed to participate in

the study. Lake ducks were obtained from commercial fishermen who found individuals entangled and drowned in gill nets at depths up to 9 m. In addition, a sample of 19 mallards (Anas platyrhynchos) were obtained from Big Creek on the Canadian mainland from hunters affiliated with the Big Creek Hunters Club. Hunter killed ducks were identified by species, age, and sex. Duck mass was determined, digestive tracts were removed for diet analysis, and liver and/or wing tissues were collected for organochlorine contaminant analysis.

Fighting island taxa collected included mallard, canvasback (Aythya valisineria), bufflehead, redhead (A. americana), and greater and lesser scaup. All individuals were collected during autumn 1993 or autumn 1994. Lake Erie greater and lesser scaup and bufflehead were collected between autumn 1993 and December 1994. Whole carcasses were recovered from commercial fishermen. Waterfowl species, age and sex were identified according to Carney (1992), and later verified by Norm North of the Canadian Wildlife Service, London, Ontario.

Diet Analysis

Contents of digestive tracts (esophagus, proventriculus and gizzard) excised from ducks were analyzed for all study ducks. Decomposition of food items, particularly in the gizzard, limited taxonomic resolution. Diet contents were categorized into three primary fractions: Dreissena, snails, and aquatic macrophytes (mainly Vallisneria) or amphipods. Contents were air dried for 72 h at 20°C. Diet contents were expressed as % dry mass.

While it is possible that the collection methods at different sites (hunting vs. gill-net drowning) may have biased diet surveys, this possibility is unlikely considering that all waterfowl were actively pursuing food acquisition when killed or drowned. All hunted ducks were in identified feeding sites when killed, while drowned individuals were often found at considerable depth in areas with Dreissena. In addition, drowned ducks often had zebra mussels visible in the mouth and esophagus.

Organochlorine Analysis

Excised wing and liver tissues from ducks were immediately wrapped in hexane-rinsed aluminum foil and frozen until analyzed. Sample preparation and gas chromatography methods follow Lazar et al. (1992)(see chapter 1). Organochlorine analysis was conducted on a total of 49 ducks based on location and diet. Of this group, both wing and liver were analyzed in 11 ducks. Lipid-normalized liver concentrations were regressed on lipid-normalized wing concentrations for these individuals. Equivalent lipid-adjusted concentrations were calculated using the regression equations described above for eight individuals for which only lipid-adjusted wing values were available. Estimates were calculated only for chemicals with explained variability (R^2) between liver and wing samples >0.70 (39 of 65 compounds). R^2 values for the 12 compounds used in statistical models (see below) ranged from 0.716 (QCB and PCB # 28) to 0.990 (PCB # 174). Contaminant concentrations were usually higher in liver than in wing tissue. The % lipid in liver ranged between 3.3 and 5.7% but did not vary among groups of waterfowl. PCB identification numbers are based on IUPAC classification system. The number of individuals analyzed for contaminants (sorted by species, location and diet) ranged between 3 and 8.

Biomagnification factors were calculated for greater and lesser scaup from Lake Erie using zebra mussels from Middle Sister Island a prey reference. BMFs were calculated as:

$$\mathrm{BMF} = [w]/[zm]$$

where [w] and [zm] are respective lipid-normalized concentrations of contaminants in waterfowl predators and Dreissena prey.

This report attempts to link current waterfowl diet profiles with contaminant patterns. Further analysis of this data set in progress, including calculation of C and N stable isotope ratios, in conjunction with the Department of Fisheries and Oceans, Canada Centre for Inland Waters. When combined with isotope profiles of food sources (Vallisneria, Dreissena, snail), it should be possible to assess long-term isotope assimilation patterns in waterfowl in relation to patterns in food sources (e.g. see Hobson et al. 1994).

Statistical Analysis

Analysis of differences in contaminant concentrations were limited to a group of four low- (HCB, OCS, QCB, PCB # 28), mid- (PCBs # 105, 118, 149, 153) and high- (PCBs # 174, 180, 194, 206) K_{OW} compounds. These compounds were selected because, within each category, correlations between chemical concentrations were low. However, substitution of other compounds for the ones included here have no material effect on results. Appendix 3.1 provides mean (1 ± S.E.) concentration values for each of the compounds analyzed.

Although many comparisons were possible to test for diet effects, we have limited our analyses to greater and lesser scaup collected at Fighting Island. These ducks were classified as mussel consumers or non-consumers based on diet analyses. A two-way ANOVA was conducted using log-(x+1) transformed, lipid-normalized chemical data to assess species and diet effects. Tests were repeated for each of QCB and PCBs # 28, 149, 153, 194 and 206 (i.e. two low-, mid- and high-K_{OW} compounds).

Location effects (lake vs. Fighting Island) were also analyzed using 2-way ANOVA using 'mussel-consuming' greater and lesser scaup from the two major collection sites. Location effects were also analyzed, separately, for Bufflehead from Lake Erie and Fighting Island, and for mallard from Big Creek and Fighting Island. The former analysis is, however, confounded by diet differences between sites.

Principal component analysis was conducted for the 12 organochlorine compounds described above. Data were log-transformed (x+1) and lipid-normalized prior to analysis. The model employed a correlation matrix and varimax rotation to generate four components (Systat 1992). Waterfowl factor scores on PC1 and PC 2 were analyzed using two-way ANOVAs (described above) to assess diet and location effects. One-way ANOVA was used to assess differences in factor scores for all ducks from Fighting Island that avoided Dreissena; Scheffé's multiple comparisons tests was used to identify waterfowl with significantly different PCA scores.

Results

Waterfowl Diet

Diets of mallard and redheads from Fighting Island and mallards from Big Creek consisted of macrophytes only (Fig. 3.1). Canvasback diets consisted of >90% macrophyte, with a small component of snail (Fig. 3.1). Bufflehead from Fighting Island also consumed primarily macrophyte (80%), and only small amounts of snail and Dreissena (Fig. 3.2). This pattern was reversed in western Lake Erie, where bufflehead consumed 69% Dreissena, 28% amphipod and no macrophyte.

Lake Erie lesser and greater scaup consumed exclusively or almost exclusively Dreissena (Figs. 3.3, 3.4). By contrast, individuals from Fighting Island could be divided into those that either mainly Dreissena or mainly macrophyte (Figs. 3.3, 3.4).

Contaminant Patterns

Concentrations of most contaminants were strongly related to diet and location (Fig. 3.5 and 3.6). For example, no contaminant averaged more than 150 µg/kg lipid in any Fighting Island duck that avoided Dreissena (Fig. 3.5), though conspecifics (bufflehead, greater and lesser scaup) that consumed Dreissena exceeded 200 µg/kg lipid for compounds including dieldrin, p,p'-DDE, OCS, and PCBs # 138, 153, 180, 201 and 206 (Fig 3.6). Diet differences both among and within sites influenced contaminant profiles and concentrations (Figs. 3.7 - 3.9). For example, ducks that consumed macrophytes and snails tended to have relatively higher concentrations of low K_{OW} compounds, while higher K_{OW} compounds were typically present in relatively higher concentrations in mussel-consuming ducks (3.5 - 3.6). Coplanar PCBs (IUPAC 77, 126, 169, 189) were present in very low concentrations in all waterfowl (see Appendix 3.1).

Mussel-consuming waterfowl had consistently higher concentrations of contaminants than conspecifics that had little or no Dreissena in their diet. As examples, relative to individuals with largely macrophyte diets, concentrations were always higher for OCS (1.9 to 38.7 x), DDE (10.5 to 16.4x) and PCBs # 153 (4.5 to 16.4x) , 180 (4.6 to 23.3x) and 206 (5.8 to 18x) in mussel-consumer scaup (Appendix 3.1). Among bufflehead, mussel consumers had concentrations of these compounds 1.5, 2.4, 5.3, 9.6 and 3.6 times higher, respectively, than conspecifics that avoided Dreissena.

Contaminant concentrations for mussel-consuming scaup did not vary by species ($p > 0.10$) or by species*site interactions ($p > 0.10$) for any of the six compounds selected as $\log K_{OW}$ representatives (QCB, PCBs # 28, 149, 153, 194, 206)(2-way ANOVAs). However, for each of these compounds excepting QCB, lake scaup had significantly higher concentrations than individuals from Fighting Island (2-way ANOVAs, $p \leq 0.01$).

Diet and species effects were explored by testing each of the six compounds in lesser and greater scaup from Fighting Island. No significant species ($p > 0.10$) or species*diet interaction effects ($p > 0.10$) were observed for any of the six compounds. However, mussel consumers had significantly ($p \leq 0.05$) higher concentrations of PCBs

153, 194 and 206 than ducks from the same site that consumed little Dreissena. Thus, only moderate to high K_{OW} compounds accumulated to a greater extent in scaup that consumed mussels (Figs. 3.8, 3.9).

Similarly, mussel-consuming bufflehead had significantly ($p<0.01$) higher concentrations of PCBs # 149, 153, 194 and 206) than conspecifics that consumed mainly macrophytes (Fig. 3.7); concentration differences among groups for low K_{OW} compounds (QCB, PCB # 28) were not significant ($p>0.10$). Finally, mallards from different sites did not vary significantly with respect to any of the six compounds tested ($p>0.10$).

Principal Component Analysis

Principal component analysis was conducted on contaminant data for 49 ducks, representing all six species, using four low-, mid- and high-K_{OW} compounds. PC 1 accounted for 44% of the original data variability, and was determined primarily by high K_{OW} compounds (PCB # 206, 153, 194, 180, 118, 105; Table 3.1). PC 2 accounted for an additional 19% of the variability and was determined by low-K_{OW} compounds (HCB, QCB). PC 3 was determined by PCBs # 149 and 174, and accounted for 18% of original data variability (Table 3.10). PC 4 was determined by PCB #28, and accounted for 10% of data variance.

Waterfowl that consumed mainly Dreissena separated on PC 1 and PC2 from those that avoided Dreissena, except for canvasbacks (Figure 3.10). Mussel-consuming and avoiding ducks had high and low PC1 scores, respectively, with ducks of mixed diet (from Fighting Island) in between these groups. Canvasbacks had the highest PC 1 score of any species that avoided Dreissena, due largely to relatively high concentrations of PCB #206 (See Appendix 3.1). However, owing to its low PC 2 score, canvasbacks separated from mussel-consuming waterfowl species.

Differences in PC 2 scores were dependent on relatively small differences in concentration of QCB (< 10 μg/kg lipid).

Two-way ANOVAs were conducted to determine whether PC 1 and 2 scores varied by species or by location for mussel-consuming ducks. No significant site (F=0.93,df=1,14, p>0.35), species (F=0.31, df=1,14, p=0.59) or site*species (F=0.94, df=1,14, p=0.35) effects were detected with respect to PC1 scores for mussel-consuming waterfowl (lesser and greater scaup) from different locations. Similarly, no significant species (F=3.01, df=1,14, p=0.10) or species*site (F=0.43, df=1,14, p=0.52) effects were observed with respect to PC 2 scores, though there was a marginally significant (F=3.92, df=1,14, p=0.068) difference in PC 2 scores by site for scaup; PC 2 scores were tended to be slightly lower for Lake Erie scaup as compared to Fighting Island individuals (Fig. 3.10).

Fighting Island greater and lesser scaup PC1 scores differed significantly (F=6.744, df=1,10, p=0.027) by diet but not by species (F=0.58, df=1,10, p=0.46) or by a diet*species interaction (F=0.15, df=1,10, p=0.70). Indeed, scores for mussel-consuming and avoiding scaup were located near opposite ends of the PC 1 axis. While macrophyte consumers differed from conspecifics that consumed mussels on this axis, their scores were very similar to those of other waterfowl taxa that avoided Dreissena. PC 2 scores of fighting island scaup did not vary by species (F=1.56, df=1,10, p=0.24), diet (F=0.89, df=1,10, p=0.37) or by an interaction (F=0.10, df=1,10, p=0.76) of these factors.

PC 1 score for Lake Erie, mussel-consuming bufflehead was significantly (F=21.5, df=1,6, p=0.004) higher than that of Fighting Island individuals that ate little Dreissena, though no difference was found with respect to PC 2 scores (F=3.51, df=1,6, p=0.11). These finding are consistent with results for other scaup (Figure 3.10).

Waterfowl that avoided Dreissena (i.e. mallard, canvasback, redhead, greater and lesser scaup) did not differ in PC1 scores (F=0.88,df=6,20, p=0.52), though differences on PC2 were significant (F=6.11, df=6,20, p=0.001). Bufflehead had significantly higher PC 2 scores than either Big Creek mallard or canvasbacks (Scheffé's test, $\alpha=0.05$).

Biomagnification factors for Lake Erie lesser and greater scaup varied tremendously across contaminants (Figure 3.11). BMFs tended to be higher for greater than for lesser scaup. In addition, BMFs were dependent on contaminant $\log K_{OW}$. For example, BMF was variable below $\log K_{OW}$ 5.8, but increased slightly with increasing $\log K_{OW}$ thereafter. Most BMFs were less than 5, though values for dieldrin, OCS, mirex and PCBs #195 and 206 were quite high (>6; Figure 3.11). The highest BMF in the study (25.5) was observed for the most hydrophobic substance (PCB # 206) studied in greater scaup.

Discussion

The Detroit River is a major entry point for organochlorine compounds into Lake Erie (Kauss and Hamdy 1985; Furlong et al. 1988). Koslowski et al. (1994) observed significant accumulations of a wide array of organochlorine compounds in the Lake Erie food web, and argued that trophic interactions may play an important role in contaminant exposure. Results from this study indicate that recent diet is a good predictor of relative contaminant concentration in lower Great Lakes' waterfowl. These patterns hold both between (lake vs. Fighting Island) and within (Fighting Island) sites. For example, ducks that consumed Dreissena tended to have elevated concentrations of most contaminants relative to conspecifics that had little or no Dreissena in the diet. At present it is not possible to determine whether these patterns are owing to disproportionate effects on contaminant concentrations of recent feeding, or whether fidelities of waterfowl to particular food types is pronounced. Consideration of stable isotope signatures for different waterfowl and putative food sources should help resolve this issue (Hobson et al. 1994).

Our study revealed very low (<10 µg/kg) concentrations of coplanar PCBs (# 77, 189, 126, 169) in all ducks, though concentration of the former two were higher in mussel consumers from Lake Erie. By contrast, Koslowski et al. (1994) reported concentrations of PCB # 77 in carp, gizzard shad, silver bass, smallmouth bass and herring gull eggs up to forty times maximum values recorded here.

Greater scaup that consumed mussels tended to have higher concentrations (and BMFs) of most contaminants than lesser scaup from the same location that also fed on Dreissena. It is not clear what factor may account for this pattern, though greater scaup ate significantly larger mussels on average than lesser scaup (Ed Mazak, pers. comm.). Because larger mussels have higher lipid-normalized contaminant concentrations (chapter 1), greater scaup may be exposed to higher levels of contaminants than lesser scaup consuming essentially the same food source. The divergence of contaminant profiles of individuals within a species at one location feeding on one food type indicates that contaminant exposure may vary both as a function of trophic position and by feeding strategy (Connolly and Pederson 1988; Evans et al. 1991; Koslowski et al. 1994). In particular, feeding strategy could greatly complicate attempts to model contaminant exposure if individuals select seemingly similar food items that in fact differ considerably in contaminant levels.

Although contaminant levels were elevated in scaup that consumed waterfowl, concentrations in these individuals are much lower than those reported for these species from the Detroit River. For example, Smith et al. (1985) reported p,p'-DDE wet weight concentrations between 8 and 13 times higher than the maximum values observed in this survey for lesser and greater scaup. Moreover, herring gulls nesting on Middle Sister Islands have total PCB concentrations at least 1 order of magnitude higher than Lake Erie scaup from this study (G. Fox, pers. comm.). Greater and lesser scaup DDE, DDT and DDD are also at least two orders of magnitude lower than values reported for eggs of double-crested cormorants, Caspian terns and Forster's tern from a variety of Great Lakes locations (Kubiak et al. 1989; Yamashita et al. 1993).

Smith et al. (1985) also reported that total PCB concentration declined with increasing lipid concentration in lesser and greater scaup and goldeneye collected in the Detroit River. No such pattern was apparent in this study, though lipid levels varied much less (3.3 -5.7%) in this study than in Smith et al.'s (~6 - 26%).

Reproductive Issues

Reproductive problems associated with organochlorine contaminants have been reported for a number of Great Lakes' waterfowl (see reviews, Fox 1993; Giesy et al. 1994). Concern has centred on the possibility that scaup that consume contaminated Dreissena in the Great Lakes may accumulate sufficient burdens of contaminants as to experience reproductive impairment. For example, European work demonstrated reduced clutch size, hatch success and chick survival rates in tufted duck fed contaminated Dreissena (de Kock and Bowmer 1992). In North America, greater scaup fly through, among other areas, the Lake Erie region during migrations to and from Alaskan breeding grounds. During 1993, greater scaup suffered an unusually high rate of reproductive failure in Alaska, only a portion of which was attributable to predators (Dr. D. Barklay, Univ. of Conn., pers. comm.). It is not known whether ducks that staged on Lake Erie and consumed Dreissena were among the group that experienced reproductive problems. However, lesser scaup chicks reared solely on a diet of zebra mussels from the Middle Sister Island area did not have highly elevated contaminant concentrations nor any evidence for high levels of stress biomarkers (C. Tessier, McGill Univ., pers. comm.). Clearly, however, additional work is warranted to identify whether greater scaup frequenting western Lake Erie experience reproductive impairment owing to consumption of contaminated Dreissena.

References

Bij, de Vaate, A. 1991. Distribution and aspects of population dynamics of the zebra mussel, Dreissena polymorpha (Pallas, 1771), in the lake IJsselmeer area (the Netherlands). Oecologia 86:40-50.

Brieger, G. and R.D. Hunter. 1993. Uptake and depuration of PCB 77, PCB 169, and hexachlorobenzene by zebra mussels (Dreissena polymorpha). Ecotoxicol. Environ. Safety 26:153-165.

Carney, S.M. 1992. Species, age and sex identification of ducks using wing plumage. U.S. Department of the Interior, U.S. Fish and Wildlife Service. Washington, D.C. 144 pp.

Cleven, E.J. and P. Frenzel. 1993. Population dynamics and production of Dreissena polymorpha (Pallas) in River Seerhein, the outlet of Lake Constance (Obersee). Arch. Hydrobiol. 127:395-407.

Connolly, P. and C.J. Pederson. 1988. A thermodynamic-based evaluation of organic chemical accumulation in aquatic organisms. Environ. Sci. Technol. 22:99-103.

de Kock, W.C. and C.T. Bowmer. 1992. Bioaccumulation, biological effects, and food chain transfer of contaminants in the zebra mussel (Dreissena polymorpha). pp. 503-533. In: T.F. Nalepa and D.W. Schloesser (eds.), Zebra Mussels. Biology, impacts, and control. Lewis Publishers, Boca Raton, Florida.

Doherty, F.G., D.W. Evans and E.F. Neuhauser. 1993. An assessment of total and leachable contaminants in zebra mussels (Dreissena polymorpha) from Lake Erie. Ecotoxicol. Environ. Safety 25:328-340.

Duursma, E.K., J. Niewenhuize and J.M. van Liere. 1984. Organochlorine contamination of the Dutch delta region as 'watched' by mussels. Wat. Sci. Tech. 16:619-622.

Evans, M.S., G.E. Noguchi and C.P. Rice. 1991. The biomagnification of polychlorinated biphenyls, toxaphene, and DDT compounds in a Lake Michigan offshore food web. Arch. Environ. Contam. Toxicol. 20:87-93.

Fisher, S.W., D.C. Gossiaux, K.A. Bruner and P.F. Landrum. 1992. Investigations of the toxicokinetics of hydrophobic contaminants in the zebra mussel (Dreissena polymorpha). pp. 465-489 In: T.F. Nalepa and D.W. Schloesser (eds.), Zebra Mussels. Biology, impacts, and control. Lewis Publishers, Boca Raton, Florida.

Fox, G.A. 1993. What have biomarkers told us about the effects of contaminants on the health of fish-eating birds in the Great Lakes? The theory and a literature review. J. Great Lakes Res. 19:722-736.

French, J.R.P. III. 1993. How well can fishes prey on zebra mussels in eastern North America. Fisheries 18:13-19.

Furlong, E.T., D.S. Carter and R.A. Hites. 1988. Organic contaminants in sediments from the Trenton Channel of the Detroit River, Michigan. J. Great Lakes Res. 14:489-501.

Geisy, J.P., J.P. Ludwig, D.E. Tillitt. 1994. Deformities in birds of the Great Lakes region. Assigning causality. Environ. Sci. Technol. 28:128-135.

Griffiths, R.W. 1992. Effects of zebra mussels (Dreissena polymorpha) on the benthic fauna of Lake St. Clair. pp. 415-437 In: T.F. Nalepa and D.W. Schloesser (eds.), Zebra Mussels. Biology, impacts, and control. Lewis Publishers, Boca Raton, Florida.

Hamilton, D.J., D. Ankney and R.C. Bailey. 1994. Predation of zebra mussels by diving ducks: an exclosure study. Ecology 75:521-531.

Hobson, K.A., J.F. Piatt and J. Pitocchelli. 1994. Using stable isotopes to determine seabird trophic relationships. J. Anim. Ecol. 63:768-798.

Holland, R.E. 1993. Changes in planktonic diatoms and water transparency in Hatchery Bay, Bass Island area, western Lake Erie since the establishment of the zebra mussel. J. Great Lakes Res. 19: 717-624.

Kauss, P.B. and Y.S. Hamdy. 1985. Biological monitoring of organochlorine contaminants in the St. Clair and Detroit Rivers using introduced clams Elliptio complanatus. J. Great Lakes Res. 11:247-263.

Koslowski, S.E., C.D. Metcalfe, R. Lazar and G.D. Haffner. 1994. The distribution of 42 PCBs, including three coplanar congeners, in the food web of the western basin of Lake Erie. J. Great Lakes Res. 20:260-270.

Kraak, M.H.S., Y.A. Wink, S.C. Stuijfzand, M.C. Buckert-de Jong, C. J. de Groot and W. Admiraal. 1994. Chronic ecotoxicology of Zn, and Pb to the zebra mussel Dreissena polymorpha. Aquat. Toxicol. 30:77-89.

Kubiak, T.J., H.J. Harris, L.M. Smith, T.R. Schwartz, D.L. Stalling, J.A. Trick, L. Sileo, D.E. Docherty and T.C. Erdman. 1989. Microcontaminants and reproductive impairment of the Forster's tern on Green Bay, Lake Michigan - 1983. Arch. Environ. Contam. Toxicol. 18:706-727.

Lazar, R., R.C. Edwards, C.D. Metcalfe, F.A.P.C. Gobas and G.D. Haffner. 1992. A simple, novel method for the quantitative analysis of coplanar polychlorinated biphenyls in the environment. Chemosphere 25:493-504.

Leach, J.H. 1992. Impacts of the zebra mussel (Dreissena polymorpha) on water quality and fish spawning reefs in western Lake Erie. pp. 381-397 In T.F. Nalepa and D.W. Schloesser (eds.), Zebra Mussels. Biology, impacts, and control. Lewis Publishers, Boca Raton, Florida.

MacIsaac, H.J. 1994. Size selective predation on zebra mussels (Dreissena polymorpha) by crayfish (Orconectes propinquus). J. North Amer. Benth. Soc. 13:206-216.

MacIsaac, H.J. Potential biotic and abiotic effects of zebra mussels on the inland waterways of North America. Amer. Zool. (in review).

Mackie G.L. 1991. Biology of the exotic zebra mussel, Dreissena polymorpha, in relation to native bivalves and its potential impact in Lake St. Clair. Hydrobiol. 219:251-268.

Marvin, C.H., B.E. McCarry and D.W. Bryant. 1994. Determination and genotoxicity of polycyclic aromatic hydrocarbons isolated from Dreissina polymorpha (zebra mussels) from Hamilton Harbour. J. Great Lakes Res. 20:523-530.

Mersch, J., E. Morhain and C. Mouvet. 1993. Laboratory accumulation and depuration of copper and cadmium in the freshwater mussel Dreissena polymorpha and the aquatic moss Rhynchostegium riparioides. Chemosphere 27:1475-1485.

Nalepa, T. 1994. Trends in zebra mussel populations in Saginaw Bay and subsequent changes in water quality. 4th International Zebra Mussel Conference, Madison, WI.

Nicholls, K.H. and G.J. Hopkins. 1993. Recent changes in Lake Erie (north shore) phytoplankton: cumulative impacts of phosphorus loading reductions and the zebra mussel introduction. J. Great Lakes. Res. 19:637-647.

Secor, C.L, E.L. Mills, J. Harshbarger, H.T. Kuntz, W.E. Gutenmann and D.J. Lisk. 1993. Bioaccumulation of toxicants, element and nutrient composition, and soft tissue histology of zebra mussels (Dreissena polymorpha) from New York state waters. Chemosphere 26:1559-1575.

Smith, V.E., J.M. Spurr, J.C. Filkins and J.J. Jones. 1985. Organochlorine contaminants of wintering ducks foraging on Detroit River sediments. J. Great Lakes Res. 11:231-246.

Stanczykowska, A., P. Zyska, A. Dombrowski, H. Kot and E. Zyska. 1990. The distribution of waterfowl in relation to mollusc populations in the man-made Lake Zegrezynskie. Hydrobiol. 191:233-240.

Stempniewicz, L. 1974. The effect of feeding of the coot (Fulica atra) on the character of the shoals of Dreissena polymorpha Pall. in the Lake Goppo. Prace Limnolog. 34:83-103.

Systat. 1992. version 5.01.Systat Inc., Evanston, IL, USA, 60201.

Wormington, A. and J.H. Leach. 1992. Concentrations of migrant ducks at Point Pelee National Park, Ontario, in response to invasion of zebra mussels, Dreissena polymorpha. Can. Field Nat. 106:376-380.

Yamashita, N., S. Tanabe, J.P. Ludwig, H. Kurita, M.E. Ludwig, and R. Tatsukawa. 1993. Embryonic abnormalities and organochlorine contamination in double-crested cormorants (Phalacrocorax auritus) and Caspian terns (Hydroprogne caspia) from the upper Great Lakes in 1988. Environ. Poll. 79:163-173.

Table 3.1 Results of PCA ordination of contaminant data for 49 waterfowl. Variable loading in bold were important determinants of principal components.

Variable Loadings (rotated)

Chemical	**PC 1**	**PC 2**	**PC 3**	**PC 4**
206	**.91**	.14	.21	.03
153	**.88**	.26	.27	.20
194	**.87**	.24	.35	.10
180	**.87**	.23	.33	.09
118	**.82**	.35	.18	.24
105	**.75**	.28	.36	.15
HCB	.51	**.76**	.17	.02
QCB	.14	**.91**	.07	.21
OCS	.48	.66	.45	-.01
149	.33	.21	**.87**	.23
174	.49	.15	**.78**	.27
28	.18	.15	.276	**.91**

Figure Legends

Figure3.1. Percentage dry mass diet composition (mean ± SE) of waterfowl from Fighting Island and Big Creek, ON. Identifiable macrophyte material was Vallisneria.

Figure 3.2. Percentage dry mass diet composition (mean ± SE) of bufflehead ducks from Fighting Island and western Lake Erie. Fighting Island ducks consumed macrophytes but no amphipods, Lake Erie ducks consumed amphipods but no macrophytes.

Figure 3.3. Mean (± SE) consumption of Dreissena, snails and macrophytes by lesser scaup from western Lake Erie and from Fighting Island. Fighting Island individuals were classified as 'plant' or 'Dreissena' consumers based on diet analysis.

Figure 3.4. Mean (± SE) consumption of Dreissena, snails and macrophytes by greater scaup from western Lake Erie and from Fighting Island. Classification as per Figure 3.3.

Figure 3.5. Lipid-adjusted mean contaminant profiles for Fighting Island waterfowl that avoided Dreissena. Each profile is based on 40 organochlorine contaminants, ranging from low K_{OW} on the left to high K_{OW} on the right. The six highest concentrations for canvasback are, from left to right, dieldrin, p,p'-DDE, and PCBs # 118, 138, 153 and 180. Patterns are similar for bufflehead except that OCS is the 3rd most abundant contaminant.

Figure 3.6. Mean contaminant profiles for Lake Erie waterfowl that consumed Dreissena as the primary or exclusive food source. The six highest concentrations in greater scaup are, from left to right, dieldrin, p,p'-DDE, OCS, and PCBs # 138 (highest), 153, 180, 201 and 206.

Figure 3.7. Mean Bufflehead contaminant profiles for individuals from Fighting Island and Lake Erie. Site differences are confounded by diet differences. See Fig. 3.5 for additional details.

Figure 3.8. Mean lesser scaup contaminant profiles for individuals from Fighting Island and Lake Erie. Fighting Island ducks were sorted by major dietary component.

Figure 3.9. Mean greater scaup contaminant profiles for individuals from Fighting Island and Lake Erie. Fighting Island ducks were sorted by major dietary component.

Figure 3.10. Mean (± 1S.E.) factor scores for waterfowl on PC 1 and PC2 from the ordination of twelve contaminants in liver tissues. Ducks are plotted by species, location and diet. Mussel-consumers had high PC1 and PC 2 scores.

Figure 3.11. Biomagnification of 40 organochlorine contaminants in lesser and greater scaup from western Lake Erie that utilized Dreissena as a primary food source. BMFs are based on lipid-adjusted values in waterfowl and Dreissena from Middle Sister Island.

Figure 3.1

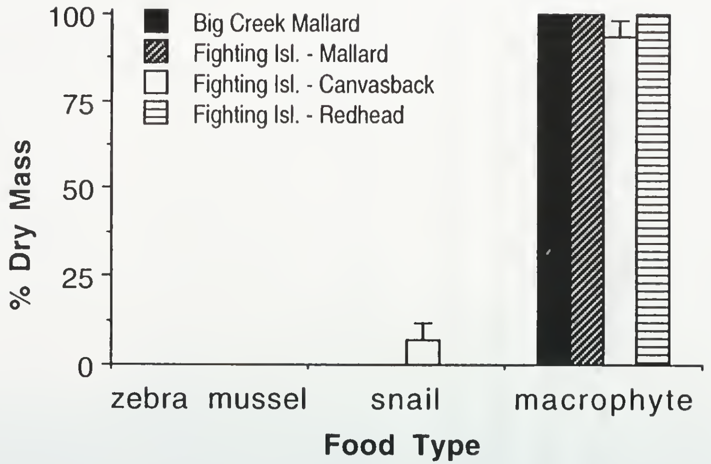

100
75
50
25
0
% Dry Mass
■ Big Creek Mallard
▨ Fighting Isl. - Mallard
☐ Fighting Isl. - Canvasback
☰ Fighting Isl. - Redhead
zebra mussel
snail
macrophyte
Food Type

Figure 3.2

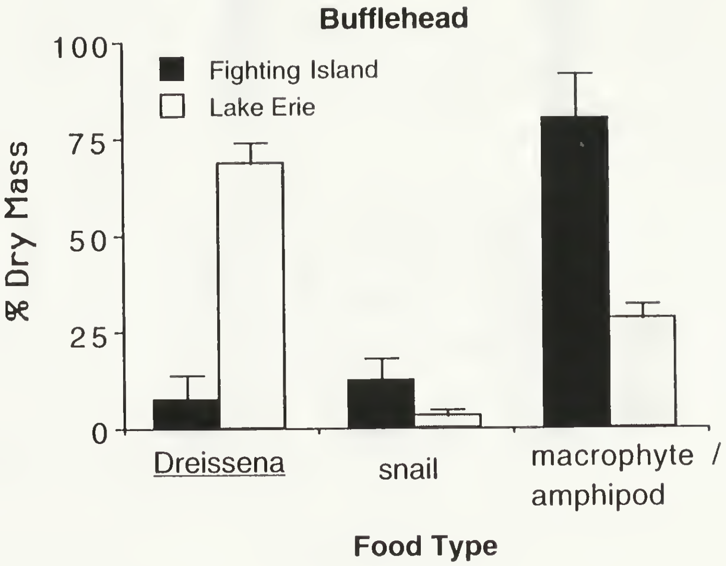

Bufflehead
Fighting Island
Lake Erie
% Dry Mass
100
75
50
25
0
Dreissena
snail
macrophyte / amphipod
Food Type

Figure 3.3

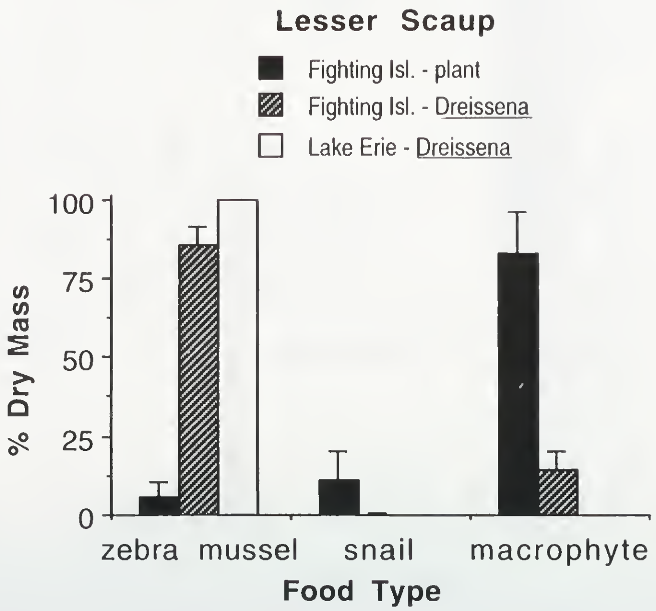

Lesser Scaup
■ Fighting Isl. - plant
▨ Fighting Isl. - Dreissena
☐ Lake Erie - Dreissena
% Dry Mass
100
75
50
25
0
zebra mussel
snail
macrophyte
Food Type

Figure 3.4

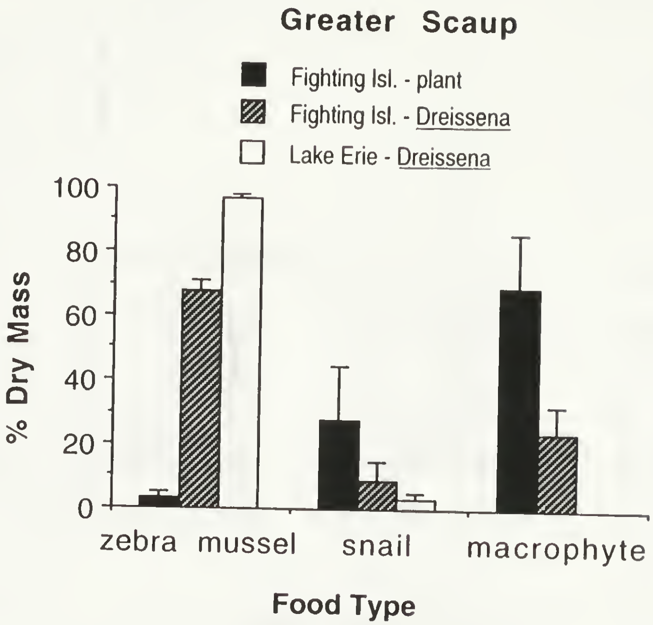
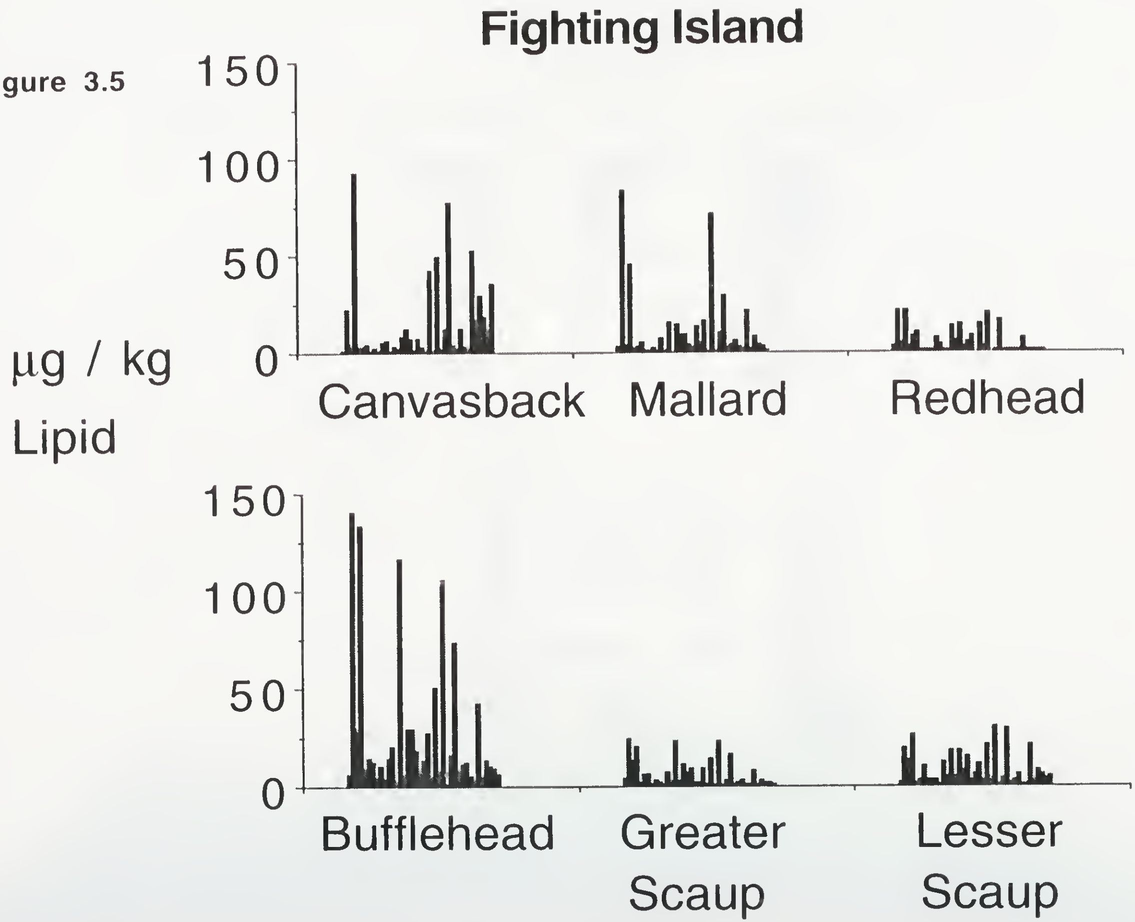

Greater Scaup
■ Fighting Isl. - plant
▨ Fighting Isl. - Dreissena
☐ Lake Erie - Dreissena
100
80
60
40
20
0
% Dry Mass
zebra mussel
snail
macrophyte
Food Type

Figure 3.5



Fighting Island

Figure 3.6

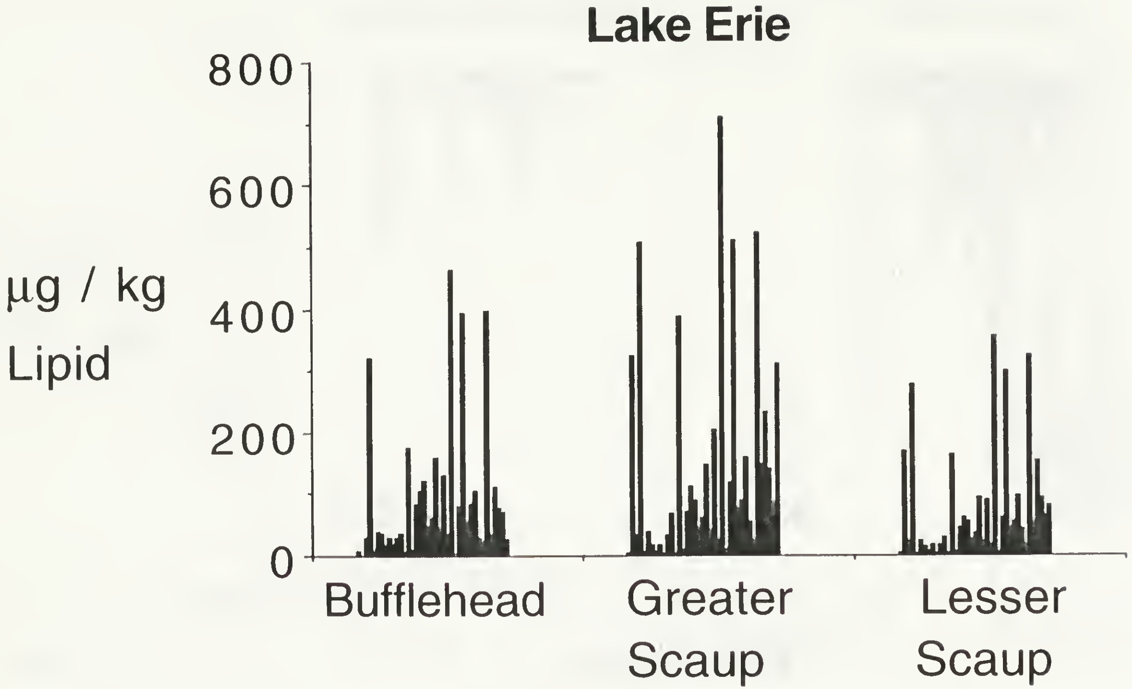
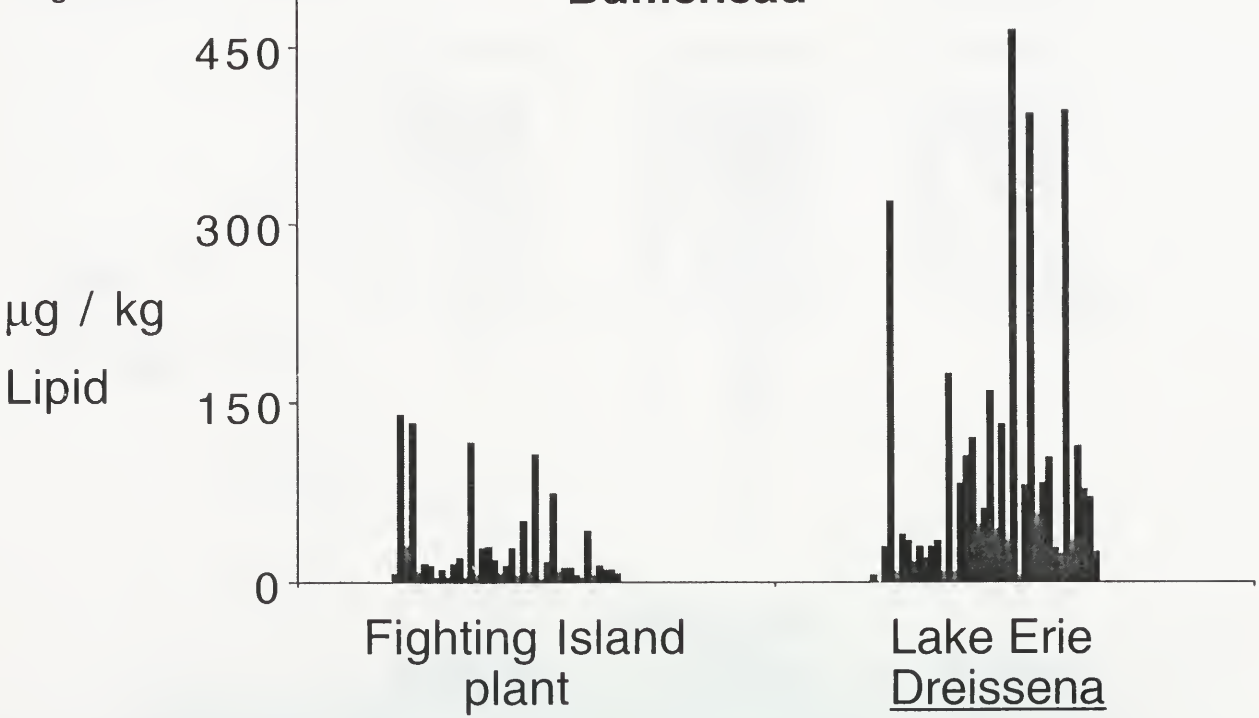

Lake Erie
µg / kg
Lipid
800
600
400
200
0
Bufflehead
Greater
Scaup
Lesser
Scaup

Figure 3.7



Bufflehead

Figure 3.8

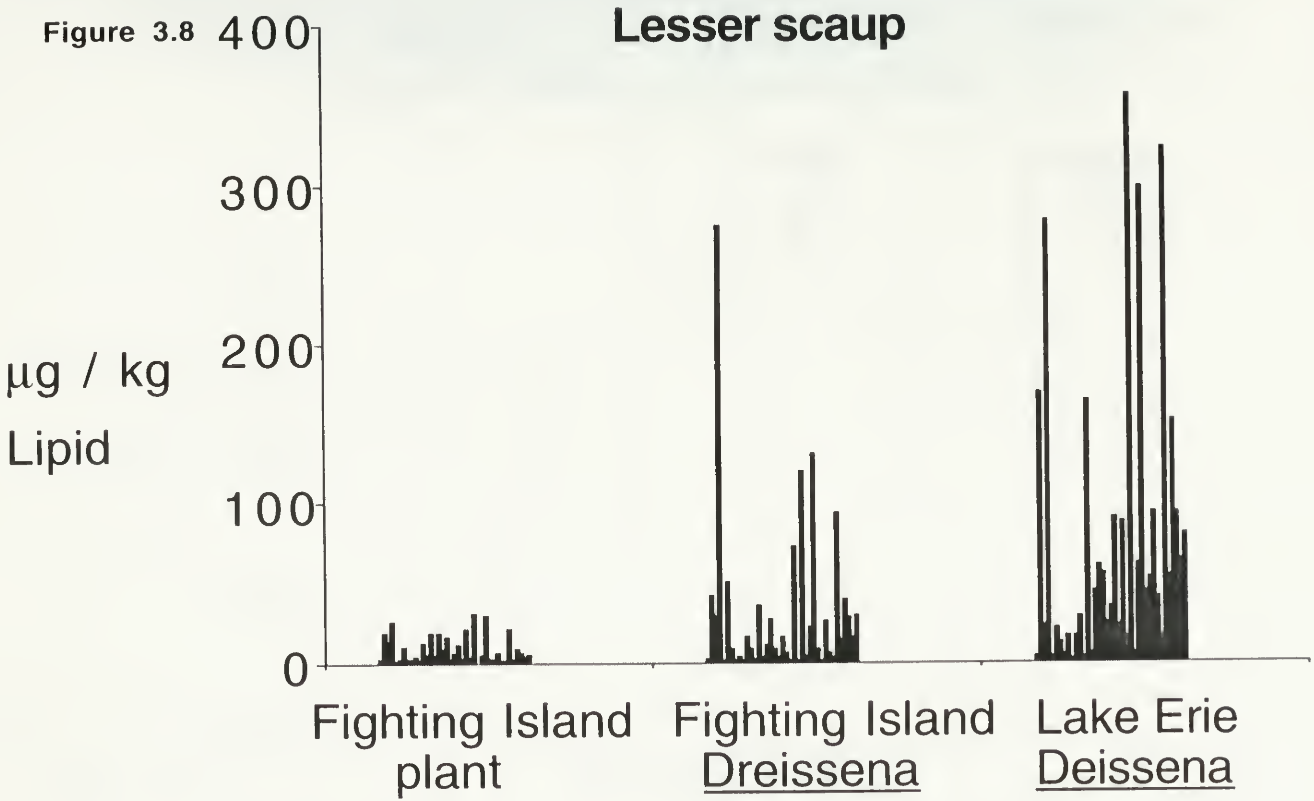
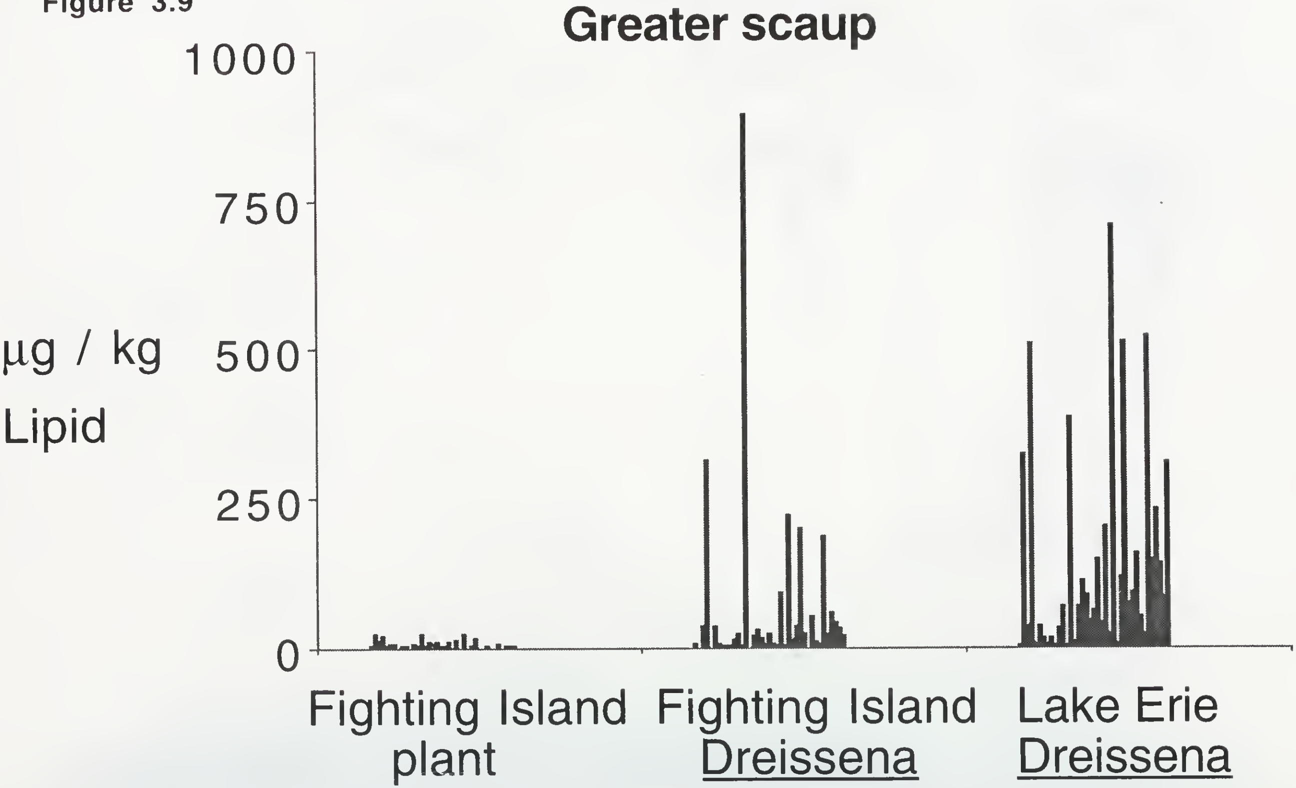

Lesser scaup
µg / kg
Lipid
400
300
200
100
0
Fighting Island plant
Fighting Island Dreissena
Lake Erie Deissena

Figure 3.9



Greater scaup

Figure 3.10

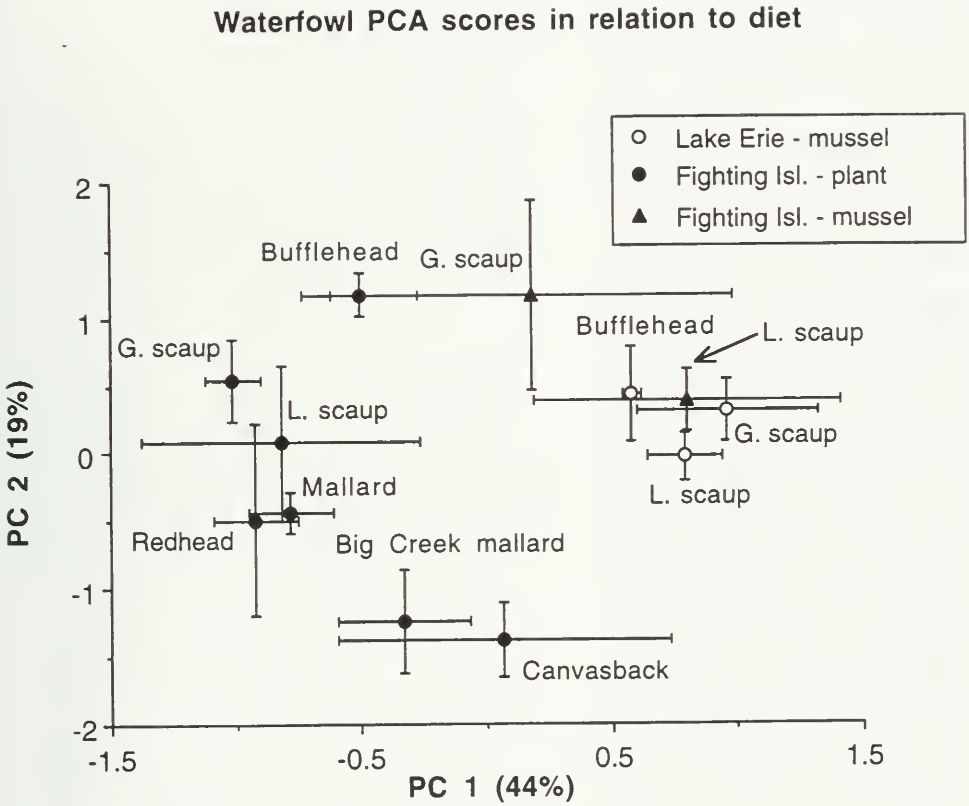
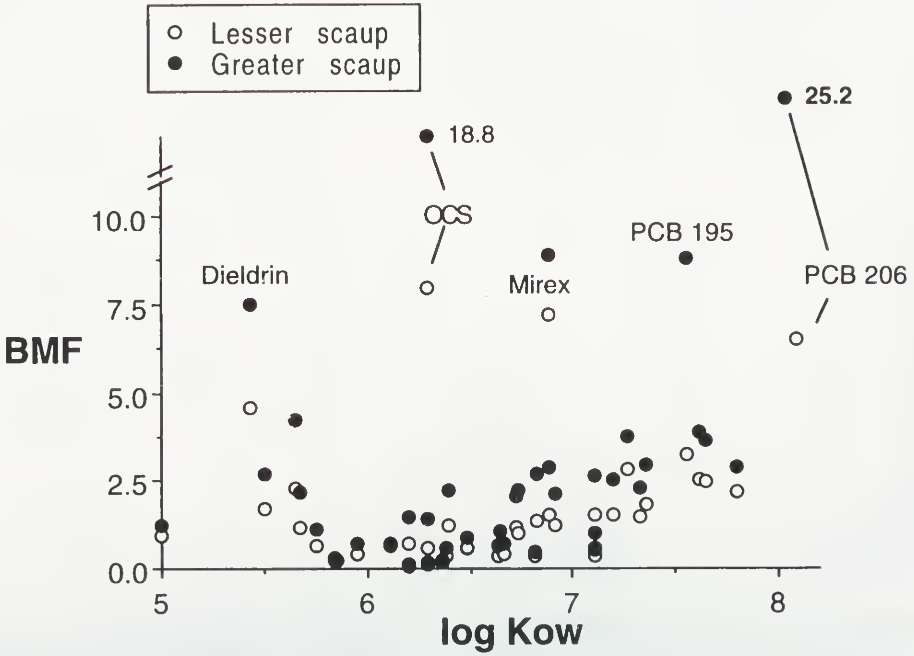

Waterfowl PCA scores in relation to diet
○ Lake Erie - mussel
● Fighting Isl. - plant
▲ Fighting Isl. - mussel
Bufflehead
G. scaup
G. scaup
L. scaup
Mallard
Redhead
Big Creek mallard
Canvasback
Bufflehead
L. scaup
G. scaup
L. scaup
PC 2 (19%)
PC 1 (44%)
2
1
0
-1
-2
-1.5
-0.5
0.5
1.5

Figure 3.11



○ Lesser scaup
● Greater scaup
18.8
25.2
OCS
PCB 195
PCB 206
Dieldrin
Mirex
BMF
10.0
7.5
5.0
2.5
0.0
5
6
7
8
log Kow

Appendix 3.1. Contaminant concentrations (Mean ± SE) for Waterfowl. Upper number is mean, lower number is S.E.

APPENDIX 3.1

MEAN +/- S.E. CONTAMINANT CONCENTRATIONS FOR ALL GROUPS OF WATERFOWL

Waterfowl Code (Site - Species - Diet)	TCB1	TCB2	OCB	HCB	OCS	aHCH	bHCH	gHCH	OXYCH	TRANSCH	CISCH	TRANSNO	CISNO	DDE	DDD	DDT	PHOTO MIREX	MIREX	HCEPOX	DIELD
Big Creek Mallard	0	1	1	4	8	1	2	1	10	0	1	4	1	45	2	1	1	1	14	18
	0	0	1	1	4	1	1	0	8	0	0	1	0	8	0	0	0	0	8	11
Fighting Isl Bufflehead	1	2	8	30	118	11	1	1	23	1	2	12	3	133	14	35	1	1	58	140
	0	1	1	3	38	3	0	0	2	0	1	3	1	28	8	19	0	0	18	40
Fighting Isl Canvasback	1	1	1	4	3	1	1	1	7	1	1	1	1	82	1	1	1	2	23	23
	0	0	0	2	1	0	0	0	5	0	0	0	0	51	0	0	0	1	12	7
Fighting Isl Great Scaup -plant	1	0	3	15	23	1	1	1	3	1	1	2	1	20	1	1	1	1	38	24
	0	0	1	2	6	0	0	0	0	0	0	0	0	3	0	0	0	0	8	8
Fighting Isl Great Scaup -Dreissena	1	1	5	30	802	1	4	1	40	1	1	4	1	514	3	1	1	11		
	0	0	2	23	814	0	3	1	30	0	0	2	0	200	2	0	0	8		
Fighting Isl Less Scaup -plant	1	1	2	15	18	3	1	1	5	1	1	2	1	20	1	0	1	1	23	10
	0	0	1	1	7	3	0	0	1	0	0	1	0	13	0	0	0	0	8	3
Fighting Isl Less Scaup -Dreissena	1	1	3	30	35	1	1	1	10	1	1	3	1	274	2	1	0	3	28	42
	0	1	1	4	12	0	0	0	6	0	0	1	0	165	1	0	0	2		
Fighting Isl Mallard	1	1	3	4	15	1	1	1	12	1	1	8	1	45	1	1	1	1	24	63
	0	0	0	1	12	0	0	0	4	0	0	3	0	32	1	0	0	0	8	47
Fighting Isl Redhead	1	1	3	5	1	1	1	1	8	1	1	2	1	21	1	1	1	0	22	21
	0	0	2	2	1	0	0	0	4	0	0	1	0	5	0	0	0	0	4	6
Lake Erie Bufflehead	0	2	5	29	173	4	1	1	18	4	7	35	8	310	50	10	0	3		
	0	0	1	7	70	1	0	0	5	0	0	4	1	65	3	1	0	1		
Lake Erie Greater Scaup	0	1	4	30	380	1	2	1	65	1	5	13	5	507	8	11	1	8	185	323
	0	0	1	12	102	0	0	0	47	0	1	5	1	313	0	2	0	8	120	117
Lake Erie Lesser Scaup	1	1	3	23	183	1	2	1	25	2	8	17	6	277	26	14	1	8	87	188
	0	0	0	3	32	0	1	0	8	1	1	3	1	81	9	2	0	1	11	25

Waterfowl Code (Site - Species - Diet)	#31	#28	#52	#49	#44	#42	#64	#74	#70	#66/95	#60	#101	#99	#97	#87	#110	#151	#149	#118	#146
Big Creek Mallard	1	4	14	3	8	1	1	8	7	17	2	26	12	7	18	22	4	14	31	5
	0	1	9	1	3	0	0	3	4	10	2	18	7	5	10	18	2	8	16	1
Fighting Isl Bufflehead	1	8	12	4	14	1	1	14	4	27	10	29	29	3	20	18	7	27	50	18
	0	3	3	1	3	0	0	7	1	7	5	5	8	1	3	7	2	8	11	5
Fighting Isl Canvasback	3	3	4	1	3	1	1	5	1	8	2	8	12	1	8	7	1	5	42	12
	2	1	3	0	1	0	0	3	1	3	1	3	7	0	5	2	0	2	29	8
Fighting Isl Great Scaup -plant	4	2	8	1	8	1	1	1	2	9	3	11	7	5	7	6	2	8	14	3
	3	0	2	1	2	0	0	0	1	1	2	2	1	1	2	2	1	2	2	1
Fighting Isl Great Scaup -Dreissena	14	1	8	2	35	1	3	15	3	17	5	18	31	5	23	15	5	7	90	37
	5	0	3	1	22	0	1	11	1	8	2	8	23	2	13	8	2	5	72	34
Fighting Isl Less Scaup -plant	3	2	10	3	3	1	1	1	3	14	1	18	8	9	12	15	3	11	21	4
	2	0	8	2	1	0	0	0	2	8	2	10	5	5	7	9	1	7	13	3
Fighting Isl Less Scaup -Dreissena	8	2	8	1	50	1	1	15	2	10	4	11	37	5	8	6	4	7	72	22
	3	1	2	1	38	0	0	11	1	1	2	2	11	1	1	2	2	4	37	6
Fighting Isl Mallard	1	2	8	1	3	1	1	1	2	6	1	14	8	1	7	8	4	13	18	10
	0	1	0	0	3	0	0	0	1	2	0	6	5	1	1	2	2	8	4	7
Fighting Isl Redhead	1	3	10	1	8	1	1	1	1	13	1	15	8	4	7	14	5	8	14	1
	0	1	2	0	1	0	0	0	0	8	0	6	5	3	8	8	2	6	6	0
Lake Erie Bufflehead	7	8	34	18	38	8	5	29	20	52	30	82	105	8	35	120	47	150	131	80
	7	3	2	1	7	1	0	5	8	5	8	8	12	1	3	8	6	12	21	12
Lake Erie Greater Scaup	1	7	18	8	37	1	3	33	5	52	18	70	110	4	67	88	45	146	202	118
	0	1	3	0	8	0	1	11	1	5	3	5	21	1	12	10	7	18	67	40
Lake Erie Lesser Scaup	1	4	12	3	21	1	2	16	3	31	15	45	80	3	28	55	24	90	87	82
	0	1	1	1	3	0	0	5	1	3	4	5	13	0	3	8	4	15	23	14

Note: All values rounded to nearest whole number

Chemical Key:

1,2,4,5-TCB = TCB1
1,2,3,4-TCB = TCB2
Pentachlorobiphenyl =OCB
Hexachlorobiphenyl =HCB
Octachlorostyrene=OCS
a-Hexachlorocyclohexane =aHCH
b-Hexachlorocyclohexane=bHCH
g-Hexachlorocyclohexane gHCH
oxy-Chlordane=oxych
trans-Chlordane=transch
cis-Chlordane=cisch
trans-Nonachlor=transno
cis-Nonachlor=cisno
p,p'-DDE=DDE
p,p'-DDT=DDT
p,p'-DDD=DDD
Dieldrin=dield
Arochlor1254 1260=A125460
Arochlor1260=A1260

	#105	#141	#138	#129	#102/187	#183	#185	#174	#171	#200	#172	#180	#170/190	#201	#203	#195	#194	#206	A 125460	A1260	#77	#126	#169	#189
Big Creek Mallard	11	6	37	3	9	4	1	4	3	1	1	14	8	6	3	2	3	1	500	119	4	1	0	0
	8	3	16	1	3	1	1	2	1	1	0	5	1	1	1	0	0	0	220	40	3	0	0	0
Fighting Isl Bufflehead	13	8	105	5	39	12	1	11	8	6	3	47	18	13	10	8	9	6	1424	368	8	1	1	1
	6	2	28	2	10	3	0	3	3	3	1	9	6	3	2	1	2	1	378	78	0	0	0	0
Fighting Isl Canvasback	7	1	49	1	30	12	1	2	4	3	2	53	20	29	18	17	13	35	660	459	3	1	1	2
	8	0	31	0	21	9	0	0	3	1	1	39	15	20	13	10	9	22	417	343	1	0	0	0
Fighting Isl Great. Scaup -plant	2	1	23	1	6	3	1	2	1	1	1	8	4	3	2	1	3	1	305	71	3	1	1	1
	1	0	4	0	1	1	0	0	0	0	0	1	1	1	1	0	1	0	49	11	1	0	0	0
Fighting Isl Great. Scaup -Dreis	22	3	221	4	140	53	1	1	24	9	7	167	83	60	41	23	33	19	2980	1643	1	1	1	
	16	1	191	3	126	49	0	0	20	7	6	173	76	65	38	20	29	15	2584	1517	1	0	0	
Fighting Isl Less. Scaup -plant	6	4	30	3	12	6	1	3	2	1	1	21	9	8	6	3	4	6	407	161	5	1	1	1
	6	2	17	2	9	6	0	2	2	0	1	19	8	8	6	2	4	4	224	166	3	0	0	0
Fighting Isl Less. Scaup -Dreiss	16	2	119	1	71	26	0	1	9	7	4	93	37	39	38	15	16	29	1610	619	4	1	1	1
	8	1	48	1	28	11	0	0	4	3	1	41	17	14	11	6	7	17	625	357	1	0	0	
Fighting Isl Mallard	3	1	71	6	42	6	1	4	3	3	3	21	11	8	4	3	3	1	963	169	0	1	1	1
	2	1	40	3	33	4	0	3	2	1	2	13	8	6	2	2	2	0	644	112	0	0	0	0
Fighting Isl Redhead	6	3	20	0	3	1	1	1	1	1	1	7	3	1	1	1	1	1	272	89	1	1	1	1
	6	2	9	0	2	0	0	0	0	0	0	2	1	0	0	0	0	0	120	17	0	0	0	0
Lake Erie Bufflehead	61	34	462	43	265	103	10	87	65	27	23	398	172	112	77	34	70	24	6241	3471	8	2	0	
	6	3	68	4	47	21	1	7	9	2	4	101	43	31	16	7	18	6	919	885	1	1	0	
Lake Erie Greater Scaup	81	24	707	47	602	158	6	90	76	64	34	620	234	232	139	148	85	310	9560	4565	9	0	1	7
	16	3	185	8	171	67	0	9	24	17	6	199	98	99	62	105	31	260	2503	1742	1	0	0	3
Lake Erie Lesser Scaup	35	16	355	33	284	94	3	57	44	41	16	322	136	150	93	64	83	80	4795	3823	8	1	1	4
	6	3	73	4	54	21	1	10	8	7	3	80	34	27	16	12	11	27	966	698	1	0	0	1